

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

DECLARATION

I, IKUO FUJINO, a Japanese Patent Attorney registered No. 9188, of Okabe International Patent Office at No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, hereby declare that I have a thorough knowledge of Japanese and English languages, and that the attached pages contain a correct translation into English of the priority documents of Japanese Patent Application No. 2000-348146 filed on November 15, 2000 in the name of CANON KABUSHIKI KAISHA.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 30th day of July, 2003



IKUO FUJINO

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy
of the following application as filed with this office.

Date of Application: November 15, 2000

Application Number: Japanese Patent Application
No. 2000-348146

Applicant(s): CANON KABUSHIKI KAISHA

Commissioner,
Patent Office

(Seal)
Certificate No.

2000-348146

[Name of the Document] Patent Application

[Reference No.] 4267016

[Date] November 15, 2000

[Addressed to] Commissioner of the
Patent Office

[International Classification] G03G 13/00
G03G 15/00

[Title of the Invention] Magnetic Toner, Image Forming
Method and Image Forming Apparatus

[Number of the Claims] 87

[Inventor]
[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] KEIJI KOMOTO

[Inventor]
[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] TSUYOSHI TAKIGUCHI

[Inventor]
[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] TATSUHIKO CHIBA

[Inventor]
[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] MICHIHISA MAGOME

[Inventor]
[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] TAKESHI KABURAGI

[Inventor]
[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] AKIRA HASHIMOTO

[Applicant]
[Identification No.] 000001007
[Name] CANON KABUSHIKI KAISHA

[Attorney]
[Identification No.] 100085006
[Patent Attorney]
[Name] KAZUNOBU SERA

[elected Attorney]
[Identification No.] 100100549
[Patent Attorney]
[Name] YOSHIYUKI KAWAGUCHI
[Telephone Number] 03-3669-6571

[elected Attorney]
[Identification No.] 100106622
[Patent Attorney]
[Name] JYUNICHI WAKUTA

[Indication of Official Fee]
[Prepayment Ledger No.] 066073
[Amount] 21000

[List of Filed Materials]
[Material] Specification 1
[Material] Drawings 1
[Material] Abstract 1

[Proof requirement] necessary

CFE3260

[Name of the Document] Specification

[Title of the Invention] Magnetic Toner, Image Forming
Method and Image Forming Apparatus

5 [Claim(s)]

[Claim 1] A magnetic toner to be used in an image
forming method, in which the image formation is
performed repeatedly on the image-bearing member,
comprising:

10 a charging step of charging an image-bearing
member comprising an electroconductive support and
photoconductor layer comprising a silicon atom-based
non-single crystal material to 250 to 600 volts in
terms of an absolute value by applying voltage to the
15 charging member abutted against the image-bearing
member while forming a contact position with the image-
bearing member;

a latent-image forming step of forming an
electrostatic latent image on the charged image-bearing
20 member;

a developing step of transferring a magnetic toner
carried on a toner-carrying member onto said
electrostatic latent image to develop the latent image,
thereby visualizing the electrostatic latent image; and

25 a transfer step of electrostatically transferring
the toner image formed on the image-bearing member onto
a transfer material,

wherein said toner contains at least a binder resin and a magnetic iron oxide, and has an average circularity of 0.920 to 0.995, 0.05 to 3.00% of isolated iron and iron compounds, and inorganic fine powder and electroconductive fine powder present at the surface.

[Claim 2] The magnetic toner according to Claim 1, wherein a particle is present in said contact position.

10 [Claim 3] The magnetic toner according to Claim 1 or 2, wherein said image-bearing member is charged to 250 to 550 volts in terms of an absolute value.

[Claim 4] The magnetic toner according to Claim 1 or 2, wherein said image-bearing member is charged to 15 250 to 500 volts in terms of an absolute value.

[Claim 5] The magnetic toner according to any one of Claims 1 to 4, wherein said magnetic toner has a weight-average particle size of 3 - 10 μm .

[Claim 6] The magnetic toner according to any one 20 of Claims 1 to 5, wherein said magnetic toner has a magnetization of 10 - 50 Am^2/kg at a magnetic field of 79.6 kA/m.

[Claim 7] The magnetic toner according to any one of Claims 1 to 6, wherein said magnetic toner contains 25 0.05 - 2.00 % of isolated iron and iron compounds.

[Claim 8] The magnetic toner according to any one of Claims 1 to 6, wherein said magnetic toner contains

0.05 - 1.50 % isolated iron and iron compounds.

[Claim 9] The magnetic toner according to any one of Claims 1 to 6, wherein said magnetic toner contains 0.05 - 0.80 % of isolated iron and iron compounds.

5 [Claim 10] The magnetic toner according to any one of Claims 1 to 9, wherein said magnetic toner has an average circularity of 0.950 to 0.995.

[Claim 11] The magnetic toner according to any one of Claims 1 to 10, wherein said magnetic toner has
10 a mode circularity of 0.970 to 0.995.

[Claim 12] The magnetic toner according to any one of Claims 1 to 11, wherein said magnetic toner has a mode circularity of at least 0.99.

[Claim 13] The magnetic toner according to any
15 one of Claims 1 to 12, wherein said magnetic iron oxide has been surface-treated in an aqueous medium with a coupling agent hydrolyzed in the medium.

[Claim 14] The magnetic toner according to any one of Claims 1 to 13, wherein said magnetic toner has
20 an inorganic fine powder with an average primary particle size of 4 - 80 nm.

[Claim 15] The magnetic toner according to any one of Claims 1 to 14, wherein said magnetic toner has the inorganic fine powder comprising at least one
25 member selected from silica, titanium oxide, and alumina with an average primary particle size of 4 - 80 nm and double oxides of these.

[Claim 16] The magnetic toner according to any one of Claims 1 to 15, wherein said magnetic toner has the inorganic fine powder which has been subjected to hydrophobicity treatment.

5 [Claim 17] The magnetic toner according to any one of Claims 1 to 16, wherein said inorganic fine powder has been treated with at least silicone oil.

[Claim 18] The magnetic toner according to any one of Claims 1 to 17, wherein said inorganic fine
10 powder has been treated with at least a silane compound and silicone oil.

[Claim 19] The magnetic toner according to any one of Claims 1 to 18, wherein said magnetic toner has a resistivity of at most 10^9 ohm.cm, and the
15 electroconductive fine powder has a volume-average particle size smaller than that of the magnetic toner and is contained in a proportion of 0.2 - 10 wt. % of the magnetic toner.

[Claim 20] The magnetic toner according to Claim
20 19, wherein said non-magnetic electroconductive fine powder has a resistivity of at most 10^6 ohm.cm.

[Claim 21] The magnetic toner according to Claim 19 or 20, wherein at least a surface portion of the non-magnetic electroconductive fine powder of said
25 magnetic toner comprises a metal oxide which contains a principal metal element and also an element different from the principal metal element in a proportion of 0.1

- 5 atom. % of the principal metal element, or a metal oxide in an oxygen-deficient state.

[Claim 22] The magnetic toner according to Claim 19 or 20, wherein said magnetic toner contains a wax in
5 a proportion of 0.1 - 20 wt. % of the magnetic toner.

[Claim 23] The magnetic toner according to Claim 22, wherein said wax has a maximum heat-absorption peak temperature of 40 - 110 °C as measured by differential scanning calorimetry.

10 [Claim 24] The magnetic toner according to Claim 22 or 23, wherein said wax has a maximum heat-absorption peak temperature of 45 - 90 °C as measured by differential scanning calorimetry.

[Claim 25] The magnetic toner according to any
15 one of Claims 1 to 24, wherein said image-bearing member is free from a means for directly warming it.

[Claim 26] The magnetic toner according to any one of Claims 1 to 25, wherein said image-bearing member has an electroconductive support, a
20 photoconductor layer comprising a silicon atom-based non-single crystal material and an uppermost layer comprising a non-single crystal material different from that of the photoconductor layer.

[Claim 27] The magnetic toner according to Claim
25 26, wherein said uppermost layer comprises a non-single crystal carbon hydride film.

[Claim 28] An image forming method, in which the

image formation is performed repeatedly on the image-bearing member, comprising:

a charging step of charging an image-bearing member;

5 a latent-image forming step of forming an electrostatic latent image on the charged image-bearing member;

a developing step of transferring a magnetic toner carried on a toner-carrying member onto said
10 electrostatic latent image to develop the latent image, thereby visualizing the electrostatic latent image; and

a transfer step of electrostatically transferring the toner image formed on the image-bearing member onto a transfer material,

15 wherein said charging step is a step of charging the image-bearing member to 250 to 600 volts in terms of an absolute value by applying voltage to the charging member abutted against the image-bearing member while forming a contact position with the image-
20 bearing member,

said image-bearing member comprises an electroconductive support and photoconductor layer comprising a silicon atom-based non-single crystal material, and

25 said toner is the magnetic toner comprising at least a binder resin and a magnetic iron oxide, and having an average circularity of 0.920 to 0.995, 0.05

to 3.00 % of isolated iron and iron compounds, and inorganic fine powder and electroconductive fine powder present at the surface.

[Claim 29] The image forming method according to
5 Claim 28, wherein a toner on the toner-carrying member in said developing step is the magnetic toner according to any one of Claims 5 to 24.

[Claim 30] The image forming method according to
Claim 28 or 29, wherein said developing step is also a
10 cleaning step of recovering a portion of the toner remaining on the image-bearing member after transferring the toner image onto the transfer material.

[Claim 31] The image forming method according to
15 any one of Claims 28 to 30, wherein said image-bearing member is primarily charged to 250 to 550 volts in terms of an absolute value.

[Claim 32] The image forming method according to
any one of Claims 28 to 31, wherein said image-bearing
20 member is primary charged to 250 to 500 volts in terms of an absolute value.

[Claim 33] The image forming method according to
any one of Claims 28 to 32, wherein said image-bearing member is free from a means for directly warming it.

25 [Claim 34] The image forming method according to
any one of Claims 28 to 33, wherein said image-bearing member has an electroconductive support, a

photoconductor layer comprising a silicon atom-based non-single crystal material and an uppermost layer comprising a non-single crystal material different from that of the photoconductor layer.

5 [Claim 35] The image forming method according to Claim 34, wherein the uppermost layer of said image-bearing member comprises a non-single crystal carbon hydride film.

 [Claim 36] The image forming method according to
10 any one of Claims 28 to 35, wherein in said charging step, a particle is present in said contact position.

 [Claim 37] The image forming method according to Claim 36, wherein in said charging step, the particle present is electroconductive fine powder.

15 [Claim 38] The image forming method according to Claim 36 or 37, wherein said charging step is the step where the image-bearing member is charged in the presence of electroconductive fine powder of 10^3 particles/mm² or more at the contact position between
20 said charging member and said image-bearing member.

 [Claim 39] The image forming method according to any one of Claims 28 to 38, wherein said charging step is the step where the image-bearing member is charged while providing a relative speed difference between
25 surface moving speeds of said charging member and said image-bearing member forming the contact position.

 [Claim 40] The image forming method according to

any one of Claims 28 to 39, wherein said charging step is the step where the image-bearing member is charged when said charging member and said image-bearing member are moved in mutually opposite directions.

5 [Claim 41] The image forming method according to any one of Claims 28 to 40, wherein said charging step is the step where the image-bearing member is charged by applying voltage to a roller member having an Asker C hardness of at most 50 deg.

10 [Claim 42] The image forming method according to any one of Claims 28 to 41, wherein said charging step is the step where the image-bearing member is charged by applying voltage to a roller member having a volume-resistivity of $10^3 - 10^8$ ohm.cm.

15 [Claim 43] The image forming method according to any one of Claims 28 to 42, wherein said charging step is the step where the image-bearing member is charged by applying voltage to a roller member and said roller member has at least a dent whose average cell diameter
20 is 5 - 300 μm in terms of sphericity on the surface and a void areal percentage on the roller member surface is 15 - 90 %, considering said dent as the void portion.

 [Claim 44] The image forming method according to any one of Claims 28 to 40, wherein said charging step
25 is the step where the image-bearing member is charged by applying voltage to an electroconductive brush member.

[Claim 45] The image forming method according to any one of Claims 28 to 44, wherein said charging step is a step in which the image-bearing member is charged by applying a DC voltage or a DC voltage with
5 superposition of an AC voltage having a peak-to-peak voltage less than $2 \times V_{th}$ relative to a discharge initiation voltage V_{th} in DC voltage application.

[Claim 46] The image forming method according to any one of Claims 28 to 45, wherein said charging step
10 is a step in which, when applying to the charging member a DC voltage or a DC voltage on which an AC voltage having a peak-to-peak voltage less than V_{th} is superposed, the image-bearing member is charged without substantially causing an electric discharge phenomenon.

15 [Claim 47] The image forming method according to any one of Claims 28 to 36, 39 and 40, wherein in said charging step, the intervening particles are magnetic particles.

[Claim 48] The image forming method according to
20 any one of Claims 28 to 36, 39, 40 and 47, wherein said charging step is the step of charging by a magnetic brush charging unit where a magnetic brush formed of magnetically constrained magnetic particles is brought into contact with the surface of said image-bearing
25 member and voltage is applied to said magnetic brush, and thereby the surface of said image-bearing member is charged.

[Claim 49] The image forming method according to Claim 47 or 48, wherein said magnetic particles have a volume-basis median diameter of 10 - 50 μm .

5 [Claim 50] The image forming method according to any one of Claims 47 to 49, wherein said magnetic particles have a volume resistivity of 1×10^4 - 1×10^9 ohm.cm.

10 [Claim 51] The image forming method according to any one of Claims 28 to 50, wherein said electrostatic latent image forming step is to write image information as an electrostatic latent image on the charged surface of the image-bearing member by image exposure.

[Claim 52] The image forming method according to any one of Claims 28 to 51, wherein said developing
15 step is the step where a toner layer of 5 - 50 g/m^2 is formed on the toner-carrying member and the toner is carried on the image-bearing member to develop the electrostatic latent image thereon.

20 [Claim 53] The image forming method according to any one of Claims 28 to 52, wherein in said developing step, the toner amount on the toner-carrying member is regulated by a ferromagnetic metal blade disposed opposite to and within a small gap from said toner-carrying member.

25 [Claim 54] The image forming method according to any one of Claims 28 to 53, wherein in said developing step, the toner-carrying member is disposed opposite to

and with a gap of 100 - 1000 μm from the image-bearing member.

[Claim 55] The image forming method according to any one of Claims 28 to 54, wherein said developing
5 step is the step where a toner layer whose thickness is smaller than a gap between the image-bearing member and the toner-carrying member is formed on the toner-carrying member and the toner is transferred from said toner layer to the image-bearing member to develop the
10 electrostatic latent image thereon.

[Claim 56] The image forming method according to any one of Claims 28 to 55, wherein said developing step is the step where a developing bias voltage comprising at least an AC voltage is applied so as to
15 form an alternating electric field between the toner-carrying member and the image-bearing member to develop an electrostatic latent image of the image-bearing member, wherein said alternating electric field has a peak-to-peak intensity of 3×10^6 - 1×10^7 V/m and a
20 frequency of 100 - 5000 Hz.

[Claim 57] The image forming method according to any one of Claims 28 to 56, wherein said transfer step is the step where a transfer member is abutted against the image-bearing member via the transfer material to
25 transfer the toner image from the image-bearing member onto the transfer material.

[Claim 58] An image forming apparatus,

comprising: an image-bearing member, a charging means for charging the image-bearing member, an electrostatic latent-image forming means forming an electrostatic latent image on the charged image-bearing member, a
5 developing means including a toner-carrying member for transferring a magnetic toner carried on the toner-carrying member onto said electrostatic latent image to visualize the electrostatic latent image thereon, and a transfer means for electrostatically transferring the
10 toner image formed on the image-bearing member onto a transfer material, for using image formation in which the image formation is performed repeatedly on the image-bearing member,

wherein said charging means comprises a charging
15 member coming in contact with said image-bearing member to form a contact portion, and is a means for charging the image-bearing member to 250 to 600 volts in terms of absolute value by applying voltage to said charging member,

20 said image-bearing member comprises an electroconductive support and a photoconductor layer comprising a non-single crystal material primarily composed of silicon atoms, and

said toner is the magnetic toner comprising at
25 least a binder resin and a magnetic iron oxide, and having an average circularity of 0.920 to 0.995, 0.05 to 3.00 % of isolated iron and iron compounds, and

inorganic fine powder and electroconductive fine powder present at the surface.

[Claim 59] The image forming apparatus according to Claim 58, wherein a toner on the toner-carrying
5 member in said developing means is the magnetic toner according to any one of Claims 5 to 24.

[Claim 60] The image forming apparatus according to Claim 58 or 59, wherein said developing means is also a cleaning step of recovering the toner remaining
10 on the image-bearing member after transferring the toner image onto the transfer material.

[Claim 61] The image forming apparatus according to any one of Claims 58 to 60, wherein said image-bearing member is charged to 250 to 550 volts in terms
15 of absolute value.

[Claim 62] The image forming apparatus according to any one of Claims 58 to 61, wherein said image-bearing member is charged to 250 to 500 volts in terms of absolute value.

20 [Claim 63] The image forming apparatus according to any one of Claims 58 to 62, wherein no means for directly heating said image-bearing member is provided.

[Claim 64] The image forming apparatus according to any one of Claims 58 to 63, wherein said image-bearing member has an electroconductive support, a
25 photoconductor layer comprising a non-single crystal material primarily composed of silicon atoms and a

uppermost layer comprising a non-single crystal material different from the photoconductor layer in its composition.

[Claim 65] The image forming apparatus according
5 to Claim 64, wherein the uppermost layer of said image-bearing member comprises a non-single crystal carbon hydride film.

[Claim 66] The image forming apparatus according to any one of Claims 58 to 65, wherein in said charging
10 means, a particle is present in said contact position.

[Claim 67] The image forming apparatus according to Claim 36, wherein in said charging step, the particle present is electroconductive fine powder.

[Claim 68] The image forming apparatus according
15 to Claim 66 or 67, wherein said charging means is the means where the image-bearing member is charged in the presence of electroconductive fine powder of 10^3 particles/mm² or more at the contact position between said charging member and said image-bearing member.

[Claim 69] The image forming apparatus according
20 to any one of Claims 58 to 68, wherein said charging means is the means where the image-bearing member is charged while providing a relative speed difference between surface moving speeds of said charging member
25 and said image-bearing member forming the contact position.

[Claim 70] The image forming apparatus according

to any one of Claims 58 to 69, wherein said charging means is the means where the image-bearing member is charged while said charging member and said image-bearing member are moved in mutually opposite
5 directions.

[Claim 71] The image forming apparatus according to any one of Claims 58 to 70, wherein said charging means is the means where the image-bearing member is charged by applying voltage to a roller member having
10 an Asker C hardness of at most 50 degrees.

[Claim 72] The image forming apparatus according to any one of Claims 58 to 71, wherein said charging means is the means where the image-bearing member is charged by applying voltage to a roller member having a
15 volume-resistivity of $10^3 - 10^8$ ohm.cm.

[Claim 73] The image forming apparatus according to any one of Claims 58 to 72, wherein said charging means is the means where the image-bearing member is charged by applying voltage to a roller member and said
20 roller member has at least a dent whose average cell diameter is 5 - 300 μm in terms of sphericity on the surface and a void areal percentage on the roller member surface is 15 - 90 % where the dent is regarded as a void portion.

25 [Claim 74] The image forming apparatus according to any one of Claims 58 to 70, wherein said charging means is the means where the image-bearing member is

charged by applying voltage to an electroconductive brush member.

[Claim 75] The image forming apparatus according to any one of Claims 58 to 74, wherein said charging
5 means is a means in which the image-bearing member is charged by applying a DC voltage or a DC voltage with superposition of an AC voltage having a peak-to-peak voltage less than $2 \times V_{th}$ relative to a discharge initiation voltage V_{th} in DC voltage application.

10 [Claim 76] The image forming apparatus according to any one of Claims 58 to 75, wherein said charging means is a means in which, when applying to charging member a DC voltage or a DC voltage on which an AC voltage having a peak-to-peak voltage less than V_{th} is
15 superposed, the image-bearing is charged without substantially causing a practical electric discharge phenomenon.

[Claim 77] The image forming apparatus according to any one of Claims 58 to 66, 69 and 70, wherein in
20 said charging means, the particles present are magnetic particles.

[Claim 78] The image forming apparatus according to any one of Claims 58 to 66, 69, 70 and 77, wherein said charging means is a means for charging by a
25 magnetic brush charging unit in which a magnetic brush formed of magnetically constrained magnetic particles is brought into contact with the surface of said image-

against the image-bearing member via the transfer material to transfer the toner image from the image-bearing member onto the transfer material.

[Detailed Description of the Invention]

5 [0001]

[Field of the Invention]

The present invention relates to a toner to be used for a recording method, such as electrophotography, electrostatic recording and
10 magnetic recording, and an image forming method and an image forming apparatus using the magnetic toner.

[0002]

[Prior Art]

Hitherto, various proposals have been made
15 regarding a toner having magnetism and image forming methods.

[0003]

U.S. Patent No. 3,908,258 has proposed a developing method using an electroconductive magnetic
20 toner, wherein an electroconductive magnetic toner is carried on an electroconductive sleeve containing a magnet therein and caused to contact an electrostatic image to effect the development. In this instance, in the developing region, an electroconductive path is
25 formed of toner particles between an image-bearing member surface and the sleeve surface, and a charge is guided from the sleeve to the toner particles via the

said toner-carrying member.

[Claim 84] The image forming apparatus according to any one of Claims 58 to 83, wherein in said developing means, the toner-carrying member is disposed
5 opposite to and with a gap of 100 - 1000 μm from the image-bearing member.

[Claim 85] The image forming apparatus according to any one of Claims 58 to 84, wherein said developing means is the means where a toner layer whose thickness
10 is smaller than a gap between the image-bearing member and the toner-carrying member is formed on the toner-carrying member and the toner is transferred from said toner layer to the image-bearing member to develop the electrostatic latent image thereon.

15 [Claim 86] The image forming apparatus according to any one of Claims 58 to 85, wherein said developing means is a means in which a developing bias voltage comprising at least an AC voltage is applied so as to form an alternating electric field between the toner-
20 carrying member and the image-bearing member to develop an electrostatic latent image of the image-bearing member, wherein said alternating electric field has a peak-to-peak intensity of 3×10^6 - 1×10^7 V/m and a frequency of 100 - 5000 Hz.

25 [Claim 87] The image forming apparatus according to any one of Claims 58 to 86, wherein said transfer means is a means in which a transfer member is abutted

bearing member and voltage is applied to said magnetic brush, and thereby the surface of said image-bearing member is charged.

[Claim 79] The image forming apparatus according
5 to Claim 77 or 78, wherein said magnetic particles have a volume-basis median diameter of 10 - 50 μm .

[Claim 80] The image forming apparatus according to any one of Claims 77 to 79, wherein said magnetic particles have a volume resistivity of 1×10^4 - 1×10^9
10 ohm.cm.

[Claim 81] The image forming apparatus according to any one of Claims 58 to 80, wherein said electrostatic latent image forming means writes image information as an electrostatic latent image on the
15 charged surface of the image-bearing member by image exposure.

[Claim 82] The image forming apparatus according to any one of Claims 58 to 81, wherein said developing means is the means where a toner layer of 5 - 50 g/m^2
20 is formed on the toner-carrying member and the toner is transferred onto the image-bearing member to develop the electrostatic latent image thereon.

[Claim 83] The image forming apparatus according to any one of Claims 58 to 82, wherein in said
25 developing means, the toner amount on the toner-carrying member is regulated by a ferromagnetic metal blade disposed opposite to and within a small gap from

electroconductive path, whereby the resultant Coulomb force acting between the toner particles and the electrostatic images causes the toner particles to attach the electrostatic image to effect a development thereof. The developing method using an electroconductive magnetic toner is an excellent method capable of obviating problems involved in a conventional two-component developing method, but on the other hand, involves a difficulty in electrostatic transfer of the developed toner image from the image-bearing member to a recording material, such as plain paper because of the electroconductivity of the toner.

[0004]

As a developing method using a high-resistivity magnetic toner which can be electrostatically transferred, there is a developing method utilizing dielectric polarization of toner particles. This method however involves problems such as an inherently slow developing speed and an insufficient developed image density, and is difficult use on a practical basis.

[0005]

As another developing method of using a high-resistivity magnetic toner, there is known a method wherein the toner particles are triboelectrically charged through friction between individual toner particles and between the toner particles and the

surface, which affect the flowability and triboelectric chargeability of the magnetic toner, and as a result, the developing characteristics of the magnetic toner as well as various characteristics required for the
5 magnetic toner such as durability will be varied or deteriorated.

[0008]

In the case of using a conventional magnetic toner containing magnetic powder, the magnetic powder exposed
10 at the magnetic toner particle surface is considered to be the major cause for the above-mentioned problem. More specifically, due to the exposure at the magnetic toner surface of fine magnetic powder having a lower resistivity than a resin constituting the toner, the
15 toners are liable to cause a lowering in chargeability, a lowering in flowability and separation of the magnetic powder due to friction or rubbing between individual toners and between the toners and a regulation member during a long term of uses, thus
20 being liable to cause an image density lowering, image density irregularity called sleeve ghost, and deterioration of the toners.

[0009]

Proposals related to magnetic iron oxide contained
25 in the magnetic toner have been made conventionally, but they still have points of improvement.

[0010]

sleeve and then caused to contact an electrostatic image on the image-bearing member to effect the development. This method involves problems such as inferior image because insufficient triboelectric charge or charging failure is liable to occur due to a relatively low frequency of contact between the toner particles and the friction member and also due to exposure of the magnetic material at the toner particle surface.

10 [0006]

JP-A 55-18656 and the like have proposed a jumping developing method, wherein a thin layer of magnetic toner is applied quite thinly and triboelectrically charged on a sleeve and is then brought to a proximity to an electrostatic image to develop the image. This method is an excellent method in that it allows a sufficient triboelectrification by the application of a magnetic toner in a thin layer on a sleeve to increase the opportunity of contact between the sleeve and the toner.

20 [0007]

However, the developing method using insulating magnetic toner has an unstable element related to the insulating magnetic toner to be used. such insulating magnetic toners are accompanied with a substantial amount of fine magnetic powder and also a portion of the magnetic powder exposed at the toner particle

For example, in JP-A 62-279352, a magnetic toner containing magnetic iron oxide comprising silicon element has been proposed. In such magnetic iron oxide, silicon element is present inside the magnetic iron oxide on purpose, but there is a still problem for flowability of the magnetic toner containing the magnetic iron oxide.

[0011]

In JP-A 3-9045, a proposal to control the shape of magnetic iron oxide to spherical by adding silicate has been made. In the magnetic iron oxide obtained by this method, many silicon elements are distributed inside the magnetic iron oxide as silicate is used for controlling the particle shape, the amount of silicon elements on the surface of the magnetic iron oxide is small, and smoothness of the magnetic iron oxide is high. Therefore, the flowability of the magnetic toner can be improved to a certain degree, but there still remains a problem that adhesion between binder resin and magnetic iron oxide constructing the magnetic toner tends to be insufficient.

[0012]

In JP-A 61-34070, a method of manufacturing Fe_3O_4 by adding hydroxyl silicate solution into the oxidative reaction to Fe_3O_4 has been proposed. In Fe_3O_4 according to this method, although there are Si elements near the surface, the Si elements exist while forming a layer

near the surface of Fe_3O_4 , thus having a problem that the surface is weak against mechanical impacts such as friction.

[0013]

5 On the other hand, toners have been manufactured by melting and mixing binder resin, coloring agent and the like, dispersing evenly, then pulverizing in a fine-powder pulverizer, and classifying using a classifying apparatus to a toner having a desired
10 particle size (pulverizing method). But there is a limitation for the range for selecting materials in order to make particle size even smaller. For example, resin coloring agent dispersing element must be sufficiently fragile and can be pulverized into fine
15 powder by a manufacturing apparatus usable from an economical viewpoint. From this demand, there is a problem that, in order to make the resin coloring agent dispersing element fragile, when this resin coloring agent dispersing element is pulverized into fine powder
20 at a high speed, particles having wide range of particle sizes tend to be formed, and especially fine particles relatively large percentage are contained here (particles pulverized excessively). Furthermore, this kind of highly fragile material is subjected to be
25 fine pulverization and degradation frequently when the material is used in a copier and the like as a toner for developing.

[0014]

In the pulverizing method, it is difficult for magnetic powders or solid fine particles such as coloring agent to disperse into resin completely
5 evenly. Poor degree of dispersion may cause increase of fog and reduction of image density. In the pulverizing method, essentially, as the magnetic iron oxide particles are exposed on the surface of the toner, the problems such as poor toner flowability and
10 charging instability under severe environment cannot be eliminated.

[0015]

More specifically, the pulverizing method has the limits for making toner particles finer required for
15 high definition and high quality image, and because of this fact, the powder characteristics, especially uniform charging capacity of the toner and flowability are substantially are decreased.

[0016]

20 In order to overcome these problems of the toners manufactured by the pulverizing method, and furthermore to meet the above-mentioned requirements, the method of manufacturing the toners using the suspension polymerization method is proposed here.

25 [0017]

A toner obtained through suspension polymerization (hereinafter referred to as a "polymerization toner")

is advantageous for high-quality image formation because of easiness of smaller particle size toner production and an improved flowability due to a sphericity of resultant toner shape.

5 [0018]

The flowability and chargeability of polymerization toners are however lowered substantially due to inclusion therein of magnetic powder (generally comprising a magnetic iron oxide). This is because
10 magnetic powder is generally hydrophilic to be predominantly present at the toner particle surface, so that a surface property modification of the magnetic powder becomes important for solving the problem.

[0019]

15 As for surface treatment of magnetic powder for improved dispersion thereof in a polymerization toner, many proposals have been made. For example, JP-A 59-200254, JP-A 59-200256, JP-A 59-200257 and JP-A 59-224102 have proposed treatment of magnetic powder with
20 various silane coupling agents, and JP-A 63-250660 and JP-A 10-239897 have disclosed treatment of silicon-containing magnetic powder with silane coupling agents.

[0020]

These treatments provide a somewhat improved
25 dispersibility in the toner but are accompanied with a problem that it is difficult to uniformly hydrophobize magnetic powder surfaces, so that it is difficult to

obviate the coalescence of magnetic powder particles and the occurrence of untreated magnetic powder particles, thus it is not enough to improve dispersibility in the toner to the satisfactory level.

5 [0021]

For printers, LED and LBP printers are the recent main stream in the market, and a technical direction is higher resolution, namely conventional 300 and 600 dpi has been improved to 400, 600, and 800 dpi. Therefore, also for the developing method, higher definition is required in accordance with this trend. In the copier segment, higher functionality has been progressed, thus heading for the direction of the digitalization. In this direction, the method of forming a latent image by laser is the mainstream, thus heading for the higher resolution as well. Here the same as the printers, the developing method with high resolution and high definition is required. For example, in JP-A 1-112253 and 2-284158, toners having smaller particle size have been proposed, but still leaving a room for considering the solutions for various problems mentioned above.

[0022]

For a toner for developing a latent image, a two-component developer comprising a carrier and toner as well as mono-component toner not requiring a carrier (magnetic toner and nonmagnetic toner) are known. For the two-component, mainly using friction between the

carrier and toner, and for the mono-component, mainly using friction between the toner and charging material, charging to the toner is conducted. For the toner, disregarding the difference between the two-component
5 and the mono-component, for the purpose of improving the toner as well as the flowability and charging characteristics of the toner, the method of adding inorganic fine powders to the toner base particles as an external additive has been proposed and widely used.

10 [0023]

For example, JP-A 5-66608, JP-A 4-9860 and the like have disclosed hydrophobized inorganic fine powder or inorganic fine powder hydrophobized and then treated with silicone oil. Further, JP-A 61-249059, JP-A 4-
15 264453 and JP-A 5-346682 have disclosed to add hydrophobized inorganic fine powder and silicone oil-treated inorganic fine powder in combination.

[0024]

Further, many proposals have been made regarding
20 addition of electroconductive fine powder as an external additive. For example, carbon black as electroconductive fine powder is widely known as an external additive to be attached to or fixed on toner particles for the purpose of, e.g., imparting
25 electroconductivity to the toner, or suppressing excessive charge of the toner to provide a uniform triboelectric charge distribution. Further, JP-A 57-

151952, JP-A 59-168458 and JP-A 60-696660 have disclosed to externally add electroconductive fine powder of tin oxide, zinc oxide and titanium oxide, respectively, to high-resistivity toner particles. JP-
5 A 56-142540 has proposed a toner provided with both developing performance and transferability by adding electroconductive magnetic particles, such as iron oxide, iron powder or ferrite, to high-resistivity magnetic toner particles so as to promote charge
10 induction to the magnetic toner. Further, JP-A 61-275864, JP-A 62-258472, JP-A 61-141452 and JP-A 02-120865 have disclosed the addition of graphite, magnetite, polypyrrole electroconductive fine powder and polyaniline electroconductive fine powder to the
15 respective toners. Further, the addition of various species of electroconductive fine powder to the toner is known.

[0025]

Conventionally, as an image forming method, many
20 methods such as electrostatic recording, magnetic recording and toner jet method are known. For example, the electrophotography generally obtains its image by the following procedure: an electric latent image is formed by various means on a photoreceptor using a
25 photoconductive material as a latent image-bearing member. Then, the latent image is developed using a toner so that it can be visualized. After transferring

the toner image onto a recording medium such as a pager, depending on its necessity, the toner image is fixed on the recording medium using heat, pressure and the like.

5 [0026]

Generally, the following image forming method has been used: the above-mentioned step is repeated via a cleaning step in which a portion of the toner remaining on the latent image-bearing member without transferring thereon after transferring is cleaned using various methods and stored in a waste toner container as a waste toner at this time.

[0027]

For the cleaning step, various methods such as blade cleaning, fur brush cleaning, and roller cleaning have been used conventionally. In any method the remaining toner after transferring is mechanically abraded down or banked up and collected into a waste toner container. Therefore, problems occurred because these members are abutted against the surface of the latent image-bearing member. For example, a member is strongly abutted against and thereby the latent image-bearing member is worn and its life becomes shorter. From the viewpoint of the apparatus size, an apparatus becomes larger by necessity as the cleaning unit should be equipped with, and the compactization of the apparatus is hampered by this. Furthermore, a system,

which does not produce a waste toner, from the perspectives of resource saving and waste reduction, effective use of the toner, as well as a system, which is excellent in fixation and offset-resistance, are
5 desired.

[0028]

On the other hand, as a system, which does not produce a waste toner, the technology called a development and simultaneous cleaning method or
10 cleanerless has been proposed.

[0029]

However, the conventionally disclosed information of the technology related to the development and simultaneous cleaning method or cleanerless mainly
15 focuses on a positive memory and a negative memory due to influences of a toner remained on an image after transferring, as shown in JP-A 5-2287. But at present, the progress of the use of the electrophotography creates a necessity for transferring a toner image onto
20 various recording media and the conventional technology is not satisfactory to use for such various media in this sense.

[0030]

The cleanerless technology is disclosed in JP-A
25 59-133573, JP-A 62-203182, JP-A 63-133179, JP-A 64-20587, JP-A 2-302772, JP-A 5-2289, JP-A 5-53482, JP-A 5-61383, etc. Such documents, however, did not

describe any desirable method of forming an image and did not refer to the toner constitution as well.

[0031]

For a step of forming a visual image using a
5 toner, various methods are known. For example, as a
method of visualizing an electrical latent image,
cascade developing, pressurized developing, and
magnetic brush developing using a two-component toner
comprising a carrier and a toner are known. In
10 addition, the following methods are also used: non-
contact mono-component developing, in which a toner-
carrying member makes a toner scattering from the
toner-carrying member to the latent image-bearing
member without contacting the latent image-bearing
15 member, magnetic one-component developing, in which a
magnetic toner and a rotary sleeve having a magnetic
pole in its center are used and the toner is scattered
in an electric field between the photosensitive member
and the sleeve, and contact mono-component developing,
20 in which the toner-carrying member is pressed onto the
latent image-bearing member and the toner is
transferred using the electrical field.

[0032]

As a developing method favorably applied in the
25 development and simultaneous cleaning or cleanerless
technology, conventionally in the development and
simultaneous cleaning method having no cleaning unit in

nature, many contact developing methods in which the toner contacts the latent image-bearing member have been considered as the structure in which the surface of the latent image-bearing member is rubbed by a toner and the toner-carrying member is essential. This is because it is considered that the configuration where the toner contacts the latent-image bearing and rubs it is more advantageous in order to recover a portion of the toner remained after transferring in a developing means. However, in the development and simultaneous cleaning method or cleanerless process applying the contact development method, toner deterioration, toner-carrying member surface deterioration, and photosensitive surface deterioration or wear are caused due to the use for long time, and problems related to durability have not been solved sufficiently. Thus, the development and simultaneous cleaning method using a non-contact development method is desired.

[0033]

For the technology to form a latent image on the image-bearing member such as electrophotographic photosensitive member and static electricity recording derivative in the image forming method used in an electrophotographic apparatus and static electricity recording apparatus, various methods are known. For example, in the electrophotography, the following method is generally used: after the photosensitive

member using a photoconductive material as the latent
image-bearing member is subjected to the charging
treatment to the specified polarity and potential
uniformly, the image pattern exposure is provided, and
5 thereby an electric latent image is formed.

[0034]

Conventionally, as a charging apparatus in which
the latent image-bearing member is charged uniformly to
the specified polarity and potential (including static
10 electricity elimination process), a corona charger
(corona discharger) has been frequently used. The
corona charger is a non-contact type charger, has a
shield electrode surrounding a discharge electrode such
as a wire electrode and this discharge electrode, is
15 provided in a non-contact manner by facing the
discharge opening portion to the image-bearing member,
and the surface of the image-bearing member is exposed
to the discharge current (corona shower) generated by
applying high voltage to the discharge electrode and
20 the shield electrode, and thereby the surface of the
image-bearing member is charged to the specified
potential.

[0035]

In recent years, a contact charging device has
25 been proposed and commercialized as a charging device
for a member to be charged such as a latent image-
bearing because of advantages, such as low ozone-

generating characteristic and a lower power consumption, than the corona charging device.

[0036]

A contact charging device is a device comprising
5 an electroconductive charging member (which may also be called a contact charging member or a contact charger in the form of a roller (charging roller), a fur brush, a magnetic brush or a blade, disposed in contact with a member-to-be-charged, such as an image-bearing member,
10 so that the contact charging member is supplied with a prescribed charging bias voltage to charge the member-to-be-charged to prescribed polarity and potential.

[0037]

The charging mechanism (or principle) during the
15 contact charging may include (1) discharge (charging) mechanism and (2) direct injection charging mechanism, and may be classified depending on which of these mechanism is predominant.

[0038]

20 (1) Discharge charging mechanism

This is a mechanism wherein a member is charged by a discharge phenomenon occurring at a minute gap between the member and a contact charging member. As a certain discharge threshold is present, it is necessary
25 to apply to the contact charging member a voltage which is larger than a prescribed potential to be provided to the member-to-be-charged. Some discharge product

occurs while the amount thereof is remarkably less than in a corona charger, and active ions, such as ozone, occur through the amount thereof is small.

[0039]

5 (2) Direct injection charging mechanism

This is a mechanism wherein a member surface is charged with a charge which is directly injected into the member from a contact charging member. This mechanism may also be called direct charging, injection
10 charging or charge-injection charging. More specifically, a charging member of a medium resistivity is caused to contact a member-to-be-charged to directly inject charges to the member-to-be-charged basically without relying on a discharge phenomenon.
15 Accordingly, a member can be charged to a potential corresponding to an applied voltage to the charging member even if the applied voltage is below a discharge threshold. This mechanism is not accompanied with occurrence of active ions, such as ozone, so that
20 difficulties caused by discharge products can be obviated. However, based on the direct injection charging mechanism, the charging performance is affected by the contactivity of the contact charging member onto the member-to-be-charged. Accordingly, it
25 is preferred to have configurations such that the charging member is provided with a more frequent contact and more dense points of contact with the

member-to-be-charged or has many types of speed differences with the member-to-be-charged.

[0040]

As a contact charging device, a roller charging
5 scheme using an electroconductive roller as a contact charging member is preferred because of the stability of charging performance and is widely used. During the contact charging according to the conventional roller charging scheme, the above-mentioned discharge charging
10 mechanism (1) is predominant. A charging roller has been formed of a conductive or medium-resistivity rubber or foam material optionally disposed in lamination to provide desired characteristics.

[0041]

15 Such a charging roller is provided with elasticity so as to ensure a certain contact with a member-to-be-charged, thus causing a large frictional resistance. The charging roller is moved following the movement of the member-to-be-charged or with a small speed
20 difference with the latter. Accordingly, even if the direct injection charging is intended, the lowering in charging performance, and charging irregularities due to insufficient contact, contact irregularity due to the roller shape and attachment onto the member-to-be-
25 charged, are liable to be caused.

[0042]

Fig. 1 is a graph illustrating examples of

charging efficiencies for charging photosensitive members by several contact charging members. The abscissa represents a bias voltage applied to the contact charging member, and the ordinate represents a resultant charged potential provided to the photosensitive member. The charging performance in the case of roller charging is represented by a line A. Thus, the surface potential of the photosensitive member starts to increase at an applied voltage exceeding a discharge threshold of ca. -500 volts. Accordingly, in order to charge the photosensitive member to a charged potential of -500 volts, for example, it is a general practice to apply a DC voltage of -1000 volts, or a DC voltage of -500 volts in superposition of an AC voltage at a peak-to-peak voltage of, e.g., 1200 volts, so as to keep a potential difference exceeding the discharge threshold, thereby causing the charged photosensitive member potential to be converged to a prescribed charged potential.

[0043]

To describe based on a specific example, in a case where a charging roller is abutted against an OPC photosensitive member having a 25 μm -thick photosensitive layer, the surface potential of the photosensitive member starts to increase in response to an applied voltage of ca. 640 volts or higher and thereafter increases linearly at a slope of 1. The

threshold voltage may be defined as a discharge inclination voltage V_{th} .

[0044]

Thus, in order to obtain a photosensitive member
5 surface potential V_d required for electrophotography,
it is necessary to apply a DC voltage of $V_d + V_{th}$
exceeding the required potential to the charging
roller. Such a charging scheme of applying only a DC
voltage to a contact charging member may be termed a
10 "DC charging scheme."

[0045]

In the DC charging scheme, however, it has been
difficult to charge the photosensitive member to a
desired potential, since the resistivity of the contact
15 charging member is liable to change in response to a
change in environmental condition, and because of a
change in V_{th} due to a surface layer thickness change
caused by abrasion of the photosensitive member.

[0046]

20 For this reason, in order to achieve a more
uniform charging, it has been proposed to adopt an "AC
charging scheme" wherein a voltage formed by
superposing a DC voltage corresponding to a desired V_d
with an AC voltage having a peak-to-peak voltage in
25 excess of $2 \times V_{th}$ is applied to a contact charging
member as described in JP-A 63-149669. According to
this scheme, the charged potential of the

photosensitive member is converged to V_d which is a central value of the superposed AC voltage due to the potential smoothing effect of the AC voltage, whereby the charged potential is not affected by the
5 environmental change.

[0047]

In the above-described contact charging scheme, the charging mechanism essentially relies on discharge from the contact charging member to the photosensitive
10 member, so that a voltage exceeding a desired photosensitive member surface potential has to be applied to the contact charging member and a small amount of ozone is generated.

[0048]

15 Further, in the AC-charging scheme for uniform charging, ozone generation is liable to be promoted, a vibration noise (AC charging noise) between the contact charging member and the photosensitive member due to AC voltage electric field is liable to be caused, and the
20 photosensitive member surface is liable to be deteriorated due to the discharge, thus posing a new problem.

[0049]

Fur brush charging is a charging scheme, wherein a
25 member (fur brush charger) comprising a brush of electroconductive fiber is used as a contact charging member, and the conductive fiber brush is in contact with

the photosensitive member is supplied with a prescribed charging bias voltage to charge the photosensitive member surface to prescribed polarity and potential. In the fur brush charging scheme, the above-mentioned
5 discharge charging mechanism (1) may be predominant.
[0050]

As the fur brush chargers, a fixed-type charger and a roller-type charger have been commercialized. The fixed type charger is formed by bonding a pile of
10 medium-resistivity fiber planted to or woven together with a substrate to an electrode. The roller-type charger is formed by winding such a pile about a core metal. A fiber density of ca. $100/\text{mm}^2$ can be relatively easily obtained, but even at such a high
15 fiber density, the contact characteristic is insufficient for realizing sufficiently uniform charging according to the direct injection charging. In order to effect a sufficiently uniform charging according to the direct injection charging, it is
20 necessary to provide a large speed difference between the fur brush charger and the photosensitive member, and not practical.
[0051]

An example of the charging performance according
25 to the fur brush charging scheme under DC voltage application is represented by a line B in Fig. 1. Accordingly, in the cases of fur brush charging using

any of the fixed-type charger and the roller-type charger, a high charging bias voltage is applied to cause a discharge phenomenon to effect the charging.
[0052]

5 In contrast to the above-mentioned charging schemes, in a magnetic brush scheme, a charging member (magnet brush charger) obtained by constraining electroconductive magnetic particles in the form of a magnetic brush under a magnetic field exerted by a
10 magnet roll is used as a contact charging member, and the magnetic brush in contact with a photosensitive member is supplied with a prescribed charging bias voltage to charge the photosensitive member surface to prescribed polarity and potential. In the magnetic
15 brush charging scheme, the above-mentioned direct injection charging scheme (2) is predominant.
[0053]

Uniform direct injection charging becomes possible, e.g., by using magnetic particles of 5-50 μm
20 in particle size and providing a sufficient speed difference with the photosensitive member. An example of the charging performance according to the magnetic brush scheme under DC voltage application is represented by a line C in Fig. 1, thus allowing a
25 charged potential almost proportional to the applied bias voltage.
[0054]

The magnetic brush charging scheme is however accompanied with difficulties that the device structure is liable to be complicated, and the magnetic particles constituting the magnetic brush are liable to be
5 liberated from the magnetic brush to be attached to the photosensitive member.

[0055]

Now, the application of such a contact charging scheme to a development and simultaneous cleaning
10 method or a cleanerless image forming method, is considered.

[0056]

The development and simultaneous cleaning method or the cleanerless image forming method does not use a
15 cleaning member, so that the transfer residual toner particles remaining on the photosensitive member are caused to contact the contact charging system wherein the discharge charging mechanism is predominant. If an insulating toner is attached to or mixed into the
20 contact charging member, the charging performance of the charging member is liable to be lowered.

[0057]

In the charging scheme wherein the discharge charging mechanism is predominant, the lowering in
25 charging performance is caused remarkably from a time when the toner layer attached to the contact charging member surface provides a level of resistance

obstructing a discharge voltage. On the other hand, in the charging scheme wherein the direct injection charging mechanism is predominant, the lowering in charging performance is caused as a lowering in chargeability of the member-to-be-charged due to a lowering in opportunity of contact between the contact charging member surface and the member-to-be-charged due to the attachment or mixing of the transfer residual toner particles into the contact charging member.

[0058]

The lowering in uniform chargeability of the photosensitive member (member-to-be-charged) results in a lowering in contrast and uniformity of latent image after imagewise exposure, and a lowering in image density and increased fog in the resultant images. Further, in the development and simultaneous cleaning method or the cleanerless image forming method, it is a point to control the charging polarity and charge of the transfer residual toner particles on the photosensitive member and stably recover the transfer residual toner particles in the developing step, thereby preventing the recovered toner from obstructing the developing performance. For this purpose, the control of the charging polarity and the charge of the transfer residual toner particles are effected by the charging member.

[0059]

This is more specifically described with respect to an ordinary laser beam printer as an example. In the case of a reversal development system using a charging member supplied with a negative voltage, a photosensitive member having a negative chargeability and a negatively charged toner, the toner image is transferred onto a recording medium in the transfer step by means of a transfer member applying a positive voltage. In this case, the transfer residual toner particles are caused to have various charges ranging from a positive polarity to a negative polarity depending on the properties (thickness, resistivity, dielectric constant, etc.) of the recording medium and the image area thereon.

[0060]

However, even if the transfer residual toner is caused to have a positive charge in the transfer step, the charge thereof can be uniformized to a negative polarity by the negatively charged charging member for negatively charging the photosensitive member. As a result, in the case of a reversal development scheme, the negatively charged residual toner particles are allowed to remain on the light-part potential where the toner is to be attached, and some irregularly charged toner attached to the dark-part potential is attracted to the toner-carrying member due to a developing

electric field relationship during the reversal development so that the transfer residual toner at the dark-part potential is not allowed to remain thereat but can be recovered. Thus, by controlling the
5 charging polarity of the transfer residual toner simultaneously with charging of the photosensitive member by means of the charging member, the development and simultaneous cleaning or cleanerless image forming method can be realized.

10 [0061]

However, if the transfer residual toner particles are attached to or mixed to the contact charging member in an amount exceeding the toner charge polarity-controlling capacity of the contact charging member,
15 the charging polarity of the transfer residual toner particles cannot be uniformized so that it becomes difficult to recover the toner particles in the developing step. Further, even if the transfer residual toner particles are recovered by a mechanical
20 force of rubbing, they adversely affect the triboelectric chargeability of the toner on the toner-carrying member if the charge of the recovered transfer residual toner particles has not been uniformized.

[0062]

25 Thus, in the development and simultaneous cleaning or cleanerless image forming method, the continuous image-forming performance and resultant image quality

are closely associated with the charge-controllability and attachment-mixing characteristic of the transfer residual toner particles at the time of passing by the charging member.

5 [0063]

Further, JP-B 7-99442 discloses to apply powder on a surface of a contact charging member contacting the member-to-be-charged so as to prevent charging irregularity and stabilize the uniform charging performance. This system however, adopts an organization of moving a contact charging member (charging roller) following the movement of the member-to-be-charged (photosensitive member) wherein the charging principle generally relies on the discharge charging mechanism simultaneously as in the above-mentioned cases of using a charging roller while the amount of ozone adduct has been remarkably reduced than in the case of using a corona charger, such as scorotron. Particularly, as an AC-superposed DC voltage is used for accomplishing a stable charging uniformity, the amount of ozone adducts is increased thereby. As a result, in the case of a continuous use of the apparatus for a long period, the defect of image flow due to the ozone products is liable to occur.

25 Further, in case where the above organization is adopted in the cleanerless image forming apparatus, the attachment of the powder onto the charging member is

obstructed by mixing with transfer-residual toner particles, thus reducing the uniform charging effect.

[0064]

Further, JP-A 5-150539 has disclosed an image forming method using a contact charging scheme wherein a developer comprising at least toner particles and electroconductive particles having an average particle size smaller than that of the toner particles is used, in order to prevent the charging obstruction due to accumulation and attachment onto the charging member surface of toner particles and silica fine particles which have not been fully removed by the action of a cleaning blade on continuation of image formation for a long period. The contact charging or proximity charging scheme used in the proposal is one relying on the discharge charging mechanism and not based on the direct injection charging mechanism so that the above problem accompanying the discharge mechanism accrues.

[0065]

Further, in case where the above organization is applied to a cleanerless image forming apparatus, larger amounts of electroconductive particles and toner particles are caused to pass through the charging step and have to be recovered in the developing step. No consideration on these matters or influence of such particles when such particles are recovered on the developing performance of the developer has been paid

in the proposal. Further, in a case where a contact charging scheme relying on the direct injection charging scheme is adopted, the electroconductive fine particles are not supplied in a sufficient quantity to
5 the contact charging member, so that the charging failure is liable to occur due to the influence of the transfer residual toner particles.

[0066]

Further, in the proximity charging scheme, it is
10 difficult to uniformly charge the photosensitive member in the presence of large amounts of electroconductive fine particles and transfer residual toner particles, thus failing to achieve the effect of removing the pattern of transfer residual toner particles. As a
15 result, the transfer residual toner particles interrupt the imagewise exposure pattern light to cause a toner particle pattern ghost. Further, in the case of instantaneous power failure or paper clogging during image formation, the interior of the image forming
20 apparatus can be remarkably soiled by the developer.

[0067]

In order to improve the charge control performance when the transfer residual toner particles are passed by the charging member in the development and
25 simultaneous cleaning method, JP-A 11-15206 has proposed to use a toner comprising toner particles containing specific carbon black and a specific azo

iron compound in mixture with inorganic fine powder. Further, it has been also proposed to use a toner having a specified shape factor and an improved transferability to reduce the amount of transfer residual toner particles, thereby improving the performance of the development and simultaneous cleaning image forming method. This image forming method however relies on a contact charging scheme based on the discharge charging scheme and not on the direct injection charging scheme, so that the system is not free from the above-mentioned problems involved in the discharge charging mechanism. Further, these proposals may be effective for suppressing the charging performance of the contact charging member due to transfer residual toner particles but cannot be expected to positively enhance the charging performance.

[0068]

Further, among commercially available electrophotographic printers, there is a type of development and simultaneous cleaning image forming apparatus including a roller member abutted against the photosensitive member at a position between the transfer step and the charging step so as to supplement or control the performance of recovering transfer residual toner particles in the development step. Such an image forming apparatus may exhibit a good

development and simultaneous cleaning performance and remarkably reduce the waste toner amount, but liable to result in an increased production cost and a difficulty against the size reduction.

5 [0069]

JP-A 10-307456 has disclosed an image forming apparatus adapted to a development and simultaneous cleaning image forming method based on a direct injection charging mechanism and using a developer
10 comprising toner particles and electroconductive charging promoter particles having particle sizes smaller than 1/2 of the toner particle size. According to this proposal, it becomes possible to provide a development and simultaneous cleaning image forming
15 apparatus which is free from generation of discharge product, can remarkably reduce the amount of waste toner and is advantageous for producing inexpensively a small size apparatus. By using the apparatus, it is possible to provide good images free from defects
20 accompanying charging failure, and interruption or scattering of imagewise exposure light. However, a further improvement is desired.

[0070]

Further, JP-A 10-307421 has disclosed an image
25 forming apparatus adapted to a development and simultaneous cleaning method, based on the direct injection charging mechanism and using a developer

containing electroconductive particles having sizes in a range of $1/50$ - $1/2$ of the toner particle size so as to improve the transfer performance.

[0071]

5 JP-A 10-307455 discloses the use of electroconductive fine particles having a particle sizes of 10 nm - 50 μm so as to reduce the particle size to below one pixel size and obtain a better charging uniformity.

10 [0072]

JP-A 10-307457 describes the use of electroconductive particles of at most about 5 μm , preferably 20 nm - 5 μm , so as to bring a part of charging failure to a visually less recognizable state in view of visual characteristic of human eyes.

[0073]

JP-A 10-307458 describes the use of electroconductive fine powder having a particle size smaller than the toner particle size so as to prevent the obstruction of toner development and the leakage of the developing bias voltage via the electroconductive fine powder, thereby removing image defects. It is also disclosed that by setting the particle size of the electroconductive fine powder to be larger than 0.1 μm , the interruption of exposure light by the electroconductive fine powder embedded at the surface of the image-bearing member is prevented to realize

excellent image formation by a development and simultaneous cleaning method based on the direct injection charging scheme.

[0074]

5 JP-A 10-307456 has disclosed a development and simultaneous cleaning image forming apparatus capable of forming good images without causing charging failure or interruption of imagewise exposure light, wherein electroconductive fine powder is externally added to a
10 toner so that the electroconductive powder is attached to the image-bearing member during the developing step and allowed to remain on the image-bearing member even after the transfer step to be present at a part of contact between a flexible contact charging member and
15 the image-bearing member.

[0075]

These proposals however have left a room for further improvement regarding the stability of performance during repetitive use for a long period and
20 performance in the case of using smaller size toner particles in order to provide an enhanced resolution.

[0076]

Further, as such members-to-be-charged, electrophotographic photosensitive members comprising
25 an Se, CdS, OPC (organic photoconductor) or an amorphous silicon (sometimes referred to as "a-Si") are known.

[0077]

An Se-based photosensitive member is a traditional photosensitive member used since the creation stage of the electrophotographic technology and is excellent in sensitivity and durability as its characteristics, thus being applied in many cases practically. At present, mainly SeTe, which has better elongation and sensitivity compared with pure selen, is mainly used, but this still has problems in heat resistance, wear resistance, mechanical strength, and stability over time, owned by the Se photosensitive member in nature. More specifically, touching by hand, breathing on, increase of temperature, and frictional contact by the cleaning device tend to cause crystallization of the photosensitive member, causing deterioration of the performance.

[0078]

Although OPC-based has put into practice thanks to the discovery of an excellent sensitizer and development of sensitizing method, this photosensitive member has a serious difficulty in wear resistance and durability, and a countermeasure thereto is urgently desired. Including the OPC photosensitive member, currently commercially available photosensitive members for use in image forming apparatus are not necessarily satisfactory in all respects of sensitivity, durability, image quality and anti-pollution

characteristic, and the weak points of respective
photosensitive members have been compensated by toner
designing or process designing to provide commercially
acceptable image forming apparatus on the market at
5 present.

[0079]

Recently, the image forming apparatuses such as
electronic copiers and laser beam printers have been
diversified as coloring, personalization, and more
10 intelligent and orient to the maintenance free. In
accordance with this trend, a photosensitive having new
characteristics and with high stability and low costs
is desired and its development has been progressed.
Under such circumstances, an a-Si attracts attention as
15 a replacement of the existing photosensitive members.

[0080]

An a-Si photosensitive member has a high
sensitivity over an entire visible wavelength region
and is therefore compatible with a semiconductor laser
20 and color image formation. Further, it has a high
surface hardness as represented by a Vickers hardness
of 1500 - 2000 kg-f/mm² and allows a long life as
represented by 5×10^5 to 10^6 or an even larger number of
sheets, several times more than a CdS photosensitive
25 member which is called to have the highest durability
and wear resistance at present. An a-Si photosensitive
member also has a heat resistance sufficient in

practical use of image forming apparatus. On the other hand of these advantages, however, the a-Si photosensitive has problems in cost reduction and mass-production.

5 [0081]

It is generally said that an a-Si photoconductor layer has a dark-part surface potential corresponding to its layer thickness. Currently commercialized photosensitive members include CdS-based showing a
10 dark-part surface potential of at least 500 volts, and Se-based and OPC-based showing dark-part surface potentials of at least 600 - 800 volts. In order to realize such a level of surface potential with an a-Si photoconductor layer, the layer thickness has to be
15 increased. Thus, in order to realize such layer thickness, the unavoidable problems of increased production cost and deteriorated production ability for the a-Si are caused. The increase of layer thickness is also liable to cause abnormal growth of the a-Si
20 layer, making the a-Si layer partially uneven, and thus being unable to use it in practical term.

[0082]

In contrast thereto, in order to provide satisfactory productivity and production costs of a-Si
25 photosensitive member and also satisfactory performance thereof, it has been proposed to form a photosensitive member having a smaller thickness of a-Si

photoconductor layer, which however, necessitates the selective use of a toner allowing a low developing potential. This is because a lower thickness of a-Si layer results in a lower surface potential than an OPC photosensitive member while it favors production cost and capacity and photosensitivity.

[0083]

Accordingly, in order to use an a-Si photosensitive member commercially satisfactorily, it is necessary to use a toner having a high developing performance. It is also necessary to control the surface property of such a small-thickness a-Si layer for providing high image quality and high durability.

[0084]

Specifically, a-Si photosensitive members comprising a non-single crystal deposition film principally comprising silicon as represented by a-Si and containing, e.g., hydrogen and/or a halogen, such as fluorine or chlorine, for compensating for hydrogen or dangling bond's have been proposed as a high-performance, high-durability and non-polluting photosensitive member, and several embodiments thereof have been commercialized. More specifically, U.S. Patent No. 4,265,991 and JP-A 54-86341 have disclosed an electrophotographic photosensitive member including a photoconductor layer principally comprising a-Si. JP-A 60-12554 has disclosed a photosensitive member

including a photoconductor layer comprising amorphous silicon and a surface layer containing carbon and halogen atoms. JP-A 2-111962 has disclosed a photosensitive member including a photosensitive layer
5 of a-Si:H or a-C:H and a surface-protecting lubrication layer. These publications are all directed to provision of a photosensitive member with improved water-repellency and wear resistance and do not relate to electrophotographic process in combination with such
10 a-Si photosensitive members.

[0085]

[Problem to be Solved by the Invention]

An object of the present invention is to provide a toner which includes the use of a magnetic toner
15 showing a stabling uniform chargeability regardless of environmental conditions and an amorphous or non-single crystal silicon photosensitive member and can provide fog-free images at high image density, good transferability and good image reproducibility for a
20 long period of use.

[0086]

Another object of the present invention is to provide an image forming method capable of providing good development and simultaneous cleaning image
25 formation while solving the above-mentioned problems.

[0087]

A further object of the present invention is to

enable a development and simultaneous cleaning image formation advantageous for cost reduction and compactization, capable of preventing the generation of discharge products, remarkably reducing the amount of waste toner, and providing a development and simultaneous cleaning image forming method and apparatus which can obtain good images free from charging failure even in a long period of repetitive use.

10 [0088]

[Means for solving the Problem]

As a result of exhaustive examination, the inventors found that the above-mentioned problems could be solved by the following magnetic toner and completed the present invention.

[0089]

The present invention is a magnetic toner to be used in an image forming method, in which the image formation is performed repeatedly on the image-bearing member, comprising a charging step of charging an image-bearing member comprising an electroconductive support and photoconductor layer comprising a silicon atom-based non-single crystal material to 250 to 600 volts in terms of an absolute value by applying voltage to the charging member abutted against the image-bearing member while forming a contact position with the image-bearing member, a latent-image forming step

of forming an electrostatic latent image on the charged image-bearing member, a developing step of transferring a magnetic toner carried on a toner-carrying member onto the electrostatic latent image to develop the latent image, thereby visualizing the electrostatic latent image; and a transfer step of electrostatically transferring the toner image formed on the image-bearing member onto a transfer material, wherein the toner contains at least a binder resin and a magnetic iron oxide, and has an average circularity of 0.920 to 0.995, 0.05 to 3.00 % of free rate of iron and iron compounds, and inorganic fine powder and electroconductive fine powder present at the surface.

[0091]

15 The present invention, as a means for solving the above-mentioned problems, provides an image forming method, in which the image formation is performed repeatedly on the image-bearing member, comprising a charging step of charging an image-bearing member; a latent-image forming step of forming an electrostatic latent image on the charged image-bearing member; a developing step of transferring a magnetic toner carried on a toner-carrying member onto the electrostatic latent image to develop the latent image, thereby visualizing the electrostatic latent image, and a transfer step of electrostatically transferring the toner image formed on the image-bearing member onto a

transfer material, wherein the charging step is a step of charging the image-bearing member to 250 to 600 volts in terms of an absolute value by applying voltage to the charging member abutted against the image-bearing member while forming a contact position with the image-bearing member, the image-bearing member comprises an electroconductive support and photoconductor layer comprising a silicon atom-based non-single crystal material, and the toner is the magnetic toner comprising at least a binder resin and a magnetic iron oxide, and having an average circularity of 0.920 to 0.995, 0.05 to 3.00 % of isolated iron and iron compounds, and inorganic fine powder and electroconductive fine powder present at the surface.

[0091]

The present invention, as a means for solving the above-mentioned problems, provides an image forming apparatus, comprising: an image-bearing member, a charging means for charging the image-bearing member, an electrostatic latent-image forming means forming an electrostatic latent image on the charged image-bearing member, a developing means including a toner-carrying member for transferring a magnetic toner carried on the toner-carrying member onto the electrostatic latent image to visualize the electrostatic latent image thereon, and a transfer means for electrostatically transferring the toner image formed on the image-

bearing member onto a transfer material, for using
image formation in which the image formation is
performed repeatedly on the image-bearing member,
wherein the charging means comprises a charging member
5 abutted against to form a contact position with the
image-bearing member, and is the means for charging the
image-bearing member to 250 to 600 volts in terms of an
absolute value by applying voltage to the charging
member, the image-bearing member comprises an
10 electroconductive support and a photoconductor layer
comprising a silicon atom-based non-single crystal
material, and the toner is the magnetic toner
comprising at least a binder resin and a magnetic iron
oxide, and having an average circularity of 0.920 to
15 0.995, 0.05 to 3.00 % of isolated iron and iron
compounds, and inorganic fine powder and
electroconductive fine powder present at the surface.
[0092]

In the present invention, it is desirable that a
20 particle is present in the contact position to improve
charging uniformity and realize stable charging
uniformity for a long period.
[0093]

In the present invention, it is preferable that
25 the image-bearing member is charged to 250 to 550
volts, and more preferably to 250 to 500 volts in terms
of an absolute value to prevent image defects.

[0094]

In the present invention, it is preferable that the magnetic toner has a weight-average particle size of 3 - 10 μm to form images with good development characteristics.

[0095]

In the present invention, it is preferable that the magnetic toner has a magnetization of 10 - 50 Am^2/kg at a magnetic field of 79.6 kA/m to prevent toner scattering and the like and form high quality images.

[0096]

In the present invention, it is preferable that the magnetic toner contains 0.05 - 2.00 %, more preferably 0.05 - 1.50 %, and even more preferably 0.05 - 0.80 % of isolated iron and iron compounds to form images with good charging characteristics.

[0097]

In the present invention, it is preferable that the magnetic toner has an average circularity of 0.950 to 0.995, and more preferably 0.970 to 0.995 to realize good transferability of the magnetic toner.

[0098]

In the present invention, it is preferable that the magnetic toner has a mode circularity of at least 0.99 to realize good charging characteristics and transferability of the magnetic toner.

[0099]

In the present invention, it is preferable that the magnetic iron oxide has been surface-treated in an aqueous medium with a coupling agent hydrolyzed in the medium to realize the above-mentioned average circularity of the magnetic toner and improve charging characteristics of the magnetic toner.

[0100]

In the present invention, it is preferable that the magnetic toner has an inorganic fine powder with an average primary particle size of 4 - 80 nm from the viewpoint of improving the flowability of the magnetic toner and more preferable that the magnetic toner has the inorganic fine powder comprising at least one member selected from silica, titanium oxide, and alumina with an average primary particle size of 4 - 80 nm and double oxides of these.

[0101]

In the present invention, it is preferable that the magnetic toner has the inorganic fine powder has been hydrophobized to control fluctuations and the like of the charging characteristics due to environmental conditions, and more preferable that the inorganic fine powder has been treated with at least silicone oil, and further preferable to be treated with at least a silane compound and silicone oil.

[0102]

In the present invention, it is preferable that the magnetic toner has a resistivity of at most 10^9 ohm.cm, and the electroconductive fine powder has a volume-average particle size smaller than that of the magnetic toner and is contained in a proportion of 0.2 - 10 wt. % of the magnetic toner to realize stable charging of the image-bearing member for a long period of time.

[0103]

10 In the present invention, it is preferable that the non-magnetic electroconductive fine powder has a resistivity of at most 10^6 ohm.cm to perform charging of the magnetic toner and charging of the image-bearing member using the charging means in a favorable range.

15 [0104]

In the present invention, it is preferable that the at least a surface portion of the non-magnetic electroconductive fine powder of the magnetic toner comprises a metal oxide which contains a principal metal element and also an element different from the principal metal element in a proportion of 0.1 - 5 atom. % of the principal metal element, or a metal oxide in an oxygen-deficient state to adjust the charging characteristics of the toner and the like.

25 [0105]

In the present invention, it is preferable that the magnetic toner contains a wax in a proportion of

0.1 - 20 wt. % of the magnetic toner to improve anti-offset property of the toner.

[0106]

In the present invention, it is preferable that
5 the wax has a maximum heat-absorption peak temperature of 40 - 110 °C and more preferably 45 - 90 °C as measured by differential scanning calorimetry to realize both high temperature anti-offset property and low temperature anti-offset property.

10 [0107]

In the present invention, it is preferable that the image-bearing member is free from a means for directly warming it to realize conservation of power consumption required for forming images and from the
15 viewpoint of reducing toner melt-sticking.

[0108]

In the present invention, it is preferable that the image-bearing member has an electroconductive support, a photoconductor layer comprising a silicon
20 atom-based non-single crystal material and a surfacemost layer comprising a non-single crystal material different from that of the photoconductor layer and the surfacemost layer comprises a non-single crystal carbon hydride film to increase the life of the
25 image-bearing member.

[0109]

In the present invention, it is preferable that

the developing step is also a cleaning step of recovering a portion of the toner remaining on the image-bearing member after transferring the toner image onto the transfer material from the viewpoints of ecology and compactization of the apparatus.

[0110]

In the present invention, it is preferable that in the charging step, the particle present is electroconductive fine powder to form high quality images in a stable manner, and more preferable that the charging step is the step where the image-bearing member is charged in the presence of electroconductive fine powder of 10^3 particles/mm² or more at the contact position between the charging member and the image-bearing member.

[0111]

In the present invention, it is preferable that the charging step is the step where the image-bearing member is charged while providing a relative speed difference between surface moving speeds of the charging member and the image-bearing member forming the contact position to realize uniform charging of the image-bearing member, and more preferable that the charging step is the step where the image-bearing member is charged when the charging member and the image-bearing member are moved in mutually opposite directions.

[0112]

In the present invention, it is preferable that the charging step is the step where the image-bearing member is charged by applying voltage to a roller
5 member having an Asker C hardness of at most 50 deg to improve contactability between the image-bearing member and charging material so that the image-bearing member can be charged more uniformly.

[0113]

10 In the present invention, it is preferable that the charging step is the step where the image-bearing member is charged by applying voltage to a roller member having a volume-resistivity of $10^3 - 10^8$ ohm.cm.

[0114]

15 In the present invention, it is preferable that the charging step is the step where the image-bearing member is charged by applying voltage to a roller member and the roller member has at least a dent whose average cell diameter is 5 - 300 μm in a spherical
20 conversion on the surface and a void areal percentage on the roller member surface is 15 - 90 %, considering the dent as the void portion.

[0115]

In the present invention, the charging step may be
25 the step where the image-bearing member is charged by applying voltage to an electroconductive brush member.

[0116]

In the present invention, it is preferable that the charging step is the step where the image-bearing member is charged by applying voltage when the charging member is supplied with a DC voltage or in
5 superposition with an AC voltage having a peak-to-peak voltage of below $2 \times V_{th}$ relative to a discharge initiation voltage V_{th} in DC voltage application to realize charging of the image-bearing member not accompanying the generation of ozone, and more
10 preferable that the charging step is the step where the image-bearing member charged when the charging member is supplied with a DC voltage or in superposition with an AC voltage having a peak-to-peak voltage of below V_{th} relative to a discharge initiation voltage V_{th} in
15 DC voltage application, without accompanying a practical electric discharge phenomenon to further realize power saving.

[0117]

In the present invention, it is preferable that
20 the charging step, the particles present are magnetic particles, and more specifically the charging step is the step of charging by a magnetic brush charging unit where a magnetic brush formed of magnetically constrained magnetic particles contacts the surface of
25 the image-bearing member and voltage is applied to the magnetic brush, and thereby the surface of the image-bearing member is charged to charge the image-bearing

member uniformly and prevent abrasion due to rubbing of the image-bearing member with the charging material.

[0118]

In the present invention, it is preferable that
5 the magnetic particles have a volume-basis median diameter of 10 - 50 μm , and more preferable that the magnetic particles have a volume resistivity of 1×10^4 - 1×10^9 ohm.cm.

[0119]

10 In the present invention, it is preferable that the electrostatic latent image forming step is to write image information as an electrostatic latent image on the charging plane of the image-bearing member by image exposure.

15 [0120]

In the present invention, it is preferable that the developing step is the step where a toner layer of 5 - 50 g/m^2 is formed on the toner-carrying member, and the toner is carried in on the image-bearing member to
20 develop the electrostatic latent image thereon, and in the developing step, the toner amount on the toner-carrying member is regulated by a ferromagnetic metal blade disposed opposite to and within a small gap from the toner-carrying member to regulate the above-
25 mentioned layer thickness while reducing deterioration of the toner.

[0121]

In the present invention, it is preferable that the developing step, the toner-carrying member is disposed opposite to and with a gap of 100 - 1000 μm from the image-bearing member, and the developing step
5 is the step where a toner layer whose thickness is smaller than a gap between the image-bearing member and the toner-carrying member is formed on the toner-carrying member and the toner is carried in from the toner layer to the image-bearing member to develop the
10 electrostatic latent image thereon to realize image formation less abrasion of the image-bearing member and deterioration of the toner.

[0122]

In the present invention, it is preferable that
15 the developing step is the step where a developing bias voltage comprising at least an AC voltage is applied so as to form an alternating electric field between the toner-carrying member and the image-bearing member to develop an electrostatic latent image of the image-
20 bearing member, wherein the alternating electric field has a peak-to-peak intensity of $3 \times 10^6 - 1 \times 10^7$ V/m and a frequency of 100 - 5000 Hz.

[0123]

In the present invention, it is preferable that
25 the transfer step is the step where a transfer member is abutted against the image-bearing member via the transfer material to transfer the toner image from the

image-bearing member onto the transfer material.

[0124]

[Embodiment(s)]

First of all a magnetic toner according to the
5 present invention will be described, and then an image
forming method and image forming apparatus using the
toner will further be described.

To describe more fully the composition of the
magnetic toner used in the present invention, it is
10 essential that the toner includes magnetic toner
particles comprising at least a binder resin and a
magnetic iron oxide, and inorganic fine powder and
electroconductive fine powder present at the surface of
the magnetic toner particles; has an average
15 circularity of 0.920 to 0.995; and contains 0.05 to
3.00 % of isolated iron-containing particles.

[0125]

If the magnetic toner has an average circularity
of at least 0.920, the surface unevenness of the
20 magnetic toner particles is alleviated to some extent
so that inorganic fine powder and electroconductive
fine powder as other components of the toner of the
present invention can be uniformly attached to the
magnetic toner particle surfaces, thus providing a
25 level of flowability suitable for use in an
electrophotographic process. Below 0.920, a sufficient
flowability is liable to be failed.

[0126]

In the image forming system of the present invention, in the case where the developing step (or means) is also used as a step (or means) for recovering
5 residual toner on the image-bearing member, the electroconductive fine powder behaves separately from the toner particles and is supplied to the charging step to promote the charging of the image-bearing member. In this instance, if the toner has an average
10 circularity below 0.920, the effective supply of the electroconductive fine powder from the toner to the charging step is liable to be hindered.

[0127]

A higher circularity of toner tends to improve the
15 image forming performances, and an average circularity of 0.950 or higher is preferred, and 0.970 or higher is more preferred.

[0128]

A toner comprising toner particles having an
20 average circularity of 0.970 or higher exhibits a very excellent transferability. This is presumably because in such a toner having a high circularity, the toner particles are caused to have a small contact area with the photosensitive member, thus resulting in a small
25 force of attachment force attributable to image force and van der Waals force onto the photosensitive member. As a result of a high transferability, the amount of

transfer residual toner is reduced, and the amount of the toner present at the pressure nip between the charging member and the photosensitive member is reduced to prevent the occurrence of toner attachment
5 onto the photosensitive member, thus remarkably reducing image defects.

[0129]

Further, toner particles having an average circularity of at least 0.970 are almost free from
10 surface edges to reduce the friction at the pressure nip between the charging member and the photosensitive member, to suppress the abrasion of the photosensitive member surface. These effects are particularly pronounced in an image forming method including a
15 contact transfer step liable to cause a hollow transfer image dropout. It is particularly preferred that the magnetic toner has a mode circularity of at least 0.99 meaning that particles having a circularity of at least 0.99 are predominant since the effect can be
20 insufficient in some cases if predominant particles have a low circularity even if the average circularity is high.

[0130]

If the magnetic toner satisfies preferable
25 features having an average circularity of at least 0.970 and a mode circularity of 0.99, toner ears formed on the toner-carrying member become fine and dense to

provide a uniform charge, so that fog is remarkably reduced.

[0131]

The average circularity and mode circularity are
5 used as quantitative measures for evaluating particle
shapes and based on values measured by using a flow-
type particle image analyzer ("FPIA-1000", manufactured
by Toa Iyou Denshi K.K.). A circularity (C_i) of each
individual particle (having a circle equivalent
10 diameter (D_{CE}) of at least 3.0 μm) is determined
according to an equation (1) below, and the circularity
values (C_i) are totaled and divided by the number of
total particles (m) to determine an average circularity
(C_a) as shown in an equation (2) below:

15 [0132]

[Mathematical Formula 1]

Formula (1)

$$\text{Circularity } (C_i) = L_0/L,$$

wherein L denotes a circumferential length of a
20 particle projection image, and L_0 denotes a
circumferential length of a circle having an area
identical to that of the particle projection image.

[Mathematical Formula 2]

Formula (2)

25 Average circularity (C_a) = $\sum_{i=1}^m C_i / m$

[0133]

Further, the mode circularity (C_{mod}) is determined by allotting the measured circularity values of individual toner particles to 61 classes in the circularity range of 0.40 - 1.00, and taking the
5 circularity of a class giving a highest frequency as a mode circularity (C_{mod}).

[0134]

For "FPIA-1000," the measurement device used in the present invention, after calculating the
10 circularity of each particle, actual calculation of an average circularity (C_a) and the measured circularity values (C_i) of the individual particles were divided into 61 classes in the circularity range of 0.40 - 1.00, and a central value of circularity of each class
15 was multiplied with a frequency of particles of the class to provide a product, which was then summed up to provide an average circularity. It has been confirmed that the thus-calculated average circularity (C_a) is substantially identical to an average circularity value
20 obtained (according to Equation (2) above) as an arithmetic mean of circularity values directly measured for individual particles without the above mentioned classification adopted for the convenience of data processing, e.g., for shortening the calculation time.

25 [0135]

More specifically, the above-mentioned FPIA measurement is performed in the following manner. Into

10 ml of water containing ca. 0.1 mg of surfactant, ca.
5 mg of toner sample is dispersed and subjected to 5
min. of dispersion by application of ultrasonic wave
(20 kHz, 50 W), to form a sample dispersion liquid
5 containing 5,000 - 20,000 particles/ μ l. The sample
dispersion liquid is subjected to the FPIA analysis for
measurement of the average circularity (Ca) and mode
circularity (Cm) with respect to particles having $D_{CE} \geq$
3.0 μ m.

10 [0136]

The average circularity (Ca) used herein is a
measure of roundness, a circularity of 1.000 means that
the toner particles have a shape of a perfect sphere,
and a lower circularity represents a complex particle
15 shape of the toner.

[0137]

Herein, only particles having a circle-equivalent
diameter ($DCE = L/\pi$) of at least 3 μ m are taken for the
circularity measurement because particles smaller than
20 3 μ m include a substantial amount of external additives
and the inclusion of such particles can distort the
circularity characteristic of toner particles.

[0138]

A toner having a mode circularity (Cmod) of at
25 least 0.990 means that most toner particles have shapes
similar to spherical form, exhibit the above-mentioned
effect more remarkably, and the transfer efficiency

becomes quite high.

[0139]

Thus, if such kind of toner will be used, the transfer efficiency becomes quite high and remaining
5 toner after transferring is reduced substantially, and thereby a portion of the toner at a contact position between the charging material and the photosensitive member is quite small amount. This makes it possible to perform stable charging, prevent melt-sticking of
10 the toner and remarkably reduce image defects.

[0140]

This effect appears more substantially in the image forming method including the contact transfer step, which is liable to cause missing during the
15 transfer.

[0141]

Furthermore, this exhibits a remarkably improved transferability even at a small particle size, which has provided a difficulty in providing an improved
20 transferability, and remarkably improves the developing performance for a low-potential latent image. It is particularly effective for development of digital minute spot latent image. This means that the magnetic toner exhibits a good matching with a amorphous silicon
25 photosensitive member essential for the image forming method of the present invention.

[0142]

If the average circularity (Ca) is below 0.920, the magnetic toner not only exhibits a lower transferability but also can exhibit a lower developing performance. On the other hand, if the average
5 circularity exceeds 0.995, the toner surface deterioration becomes noticeable, thus posing a problem in durability.

[0143]

Next, the percentage of isolated iron and iron
10 compounds will be described. The isolated iron and iron compounds are rate of numbers of magnetic iron oxide particles isolated from toner particles. The isolation percentage can also be determined by observation through, e.g., a scanning electron
15 microscope but may conveniently be determined by plasma-induced particle luminescence spectra. According to the latter measurement method, the percentage of isolated iron-containing particles (Fe.iso (%)) is determined based on the frequency of
20 atomic luminescence (abbreviated as "AL") of Fe separate or simultaneous with C (carbon) atomic luminescence and calculated according to the following formula:

[Mathematical Formula 3]

$$\begin{aligned} & \text{Fe.iso}(\%) \\ &= 100 \times \{ \text{number of AL of Fe alone} \} / \{ \text{number of AL} \\ & \quad \text{of Fe simultaneous with AL of C} \} + \{ \text{number of AL} \end{aligned}$$

of Fe alone))

[0144]

In this instance, AL of Fe is regarded as simultaneous if it occurs within 2.6 m.sec from AL of C, and regarded as separate if it occurs thereafter. As many magnetic iron oxide particles as magnetic powders are contained in the present invention, it is possible rephrase that the simultaneous luminescence of carbon atom and iron atom means a luminescence from a toner particle containing magnetic powder dispersed therein, and the luminescence of only iron atom means a luminescence from an isolated magnetic powder from the toner.

[0145]

In the plasma-induced luminescence measurement method, fine particles like toner particles are introduced into plasma, particle by particle, to determine an element and a particle size of a luminescent particle from its luminescence spectrum. For example, in the case where a magnetic toner particle is introduced into plasma, each toner particle causes one luminescence of carbon (constituting the binder resin) and one luminescence of iron (constituting the magnetic iron oxide) which can be respectively observed. As one toner particle causes one luminescence, the number of toner particles can be determined based on the number of observed

luminescences (C with Fe). The measurement may be performed by using e.g., a particle analyzer ("PT1000", made by Yokogawa Denki K.K.) according to a principle described in Japan Hardcopy '97 Paper Collection, pp.

5 65 - 68.

[0146]

More specifically, for the measurement, a sample toner left standing overnight in an environment of 23 °C and 60 %RH is subjected to measurement together with
10 0.1 % O₂-containing helium gas in the above environment. For spectrum separation, Channel 1 detector is used for carbon atom (at wavelength of 247.86 nm, with a recommended value of K factor) and Channel 2 detector is used for iron atom (at wavelength
15 of 239.56 nm, with K factor of 3.3764). Sampling is performed at a rate of one scan for covering 1000 - 1400 times of luminescence of carbon atom, and the sampling is repeated until the luminescences of carbon atom reaches at least 10,000 times. By integrating the
20 luminescences, a particle size distribution curve is drawn with the number of luminescences taken on the ordinate and with the cube root of voltage representing a particle size on the abscissa, while effecting the sampling so that the particle size distribution curve
25 exhibits a single peak and no valley. Based on the measured data while taking noise cut level during the measurement at 1.50 volts, Fe.iso (%) is calculated

according to the above formula.

[0147]

Incidentally, any material other than an inorganic compound containing iron atom such as an azo-iron
5 compound as a charge control agent may be contained in a toner in some cases, but in the azo-iron compound carbon in organic compound also emits light simultaneously with iron atom, thus it is not counted as an isolated iron atom.

10 [0148]

As a result of our study, there is found a close correlation between the percentage of isolated iron containing particles (Fe.iso (%)) and the rate of exposure of magnetic materials at the toner particle
15 surfaces. More specifically, it was discovered that if Fe.iso (%) is at most 3.00 %, the exposure at the toner particle surfaces of magnetic materials is almost suppressed to provide a high chargeability. This is attributable to the uniformity of particle size
20 distribution of the magnetic materials and uniformity of treatment. For example, in case where the surface treatment of the magnetic materials is not uninformed, magnetic materials due to insufficient surface treatment (having a high hydrophillicity) are exposed
25 to the toner particle surface, and a portion or all of them can be isolated from the toner surface layer.

[0149]

Accordingly, a toner containing a lower percentage of isolated iron-containing particles tends to show a higher chargeability. On the other hand, if Fe.iso (%) is higher than 3.00 %, the charge-leakage points are increased, thus being liable to result in a toner having an insufficient chargeability. This tendency becomes particularly remarkable in a high temperature/high humidity environment. A toner having a low chargeability is not desirable because it causes increased fog, causes a lower transferability and is liable to cause charging failure. Further, a toner satisfying both a high average circularity and a low percentage of isolated iron-containing particles can acquire a high chargeability and also a very high transferability as a result of synergy with the toner particle shape.

[0150]

On the other hand, an Fe-iso (%) of below 0.05 % means that substantially no magnetic materials are isolated from the toner. Such a magnetic toner having a low Fe.iso (%) has a high chargeability but is liable to cause an excessive charge resulting in images having a low image density and accompanied with roughening, in image formation on a large number of sheets, particularly in a low temperature/low humidity environment.

[0151]

This is presumably because of the following mechanism.

A toner carried on a toner-carrying member is not wholly transferred for development onto the
5 photosensitive member, but some toner remains on the toner-carrying member even immediately after the development. This tendency is particularly noticeable in the jumping developing mode using a toner, but the developing efficiency is not that high. Further, toner
10 particles having a high circularity, as mentioned above, form uniformly thin ears in the developing regions, and toner particles present at the tips of ears are used for development and toner particles present close to the toner-carrying member are not
15 readily consumed for the development.

[0152]

As a result, this ends up to vicious cycle where the toner particles close to the toner-carrying member are liable to be excessively charged due to repetitive
20 tribo-electrification with the charging members, and the transfer for development thereof becomes further difficult. In such a state, the charge uniformity of the toner is impaired, to result in rough images.

[0153]

25 Now, if a toner having Fe.iso (%) ≥ 0.05 % is used, the excessive charge of the toner is suppressed due to the isolated magnetic materials and magnetic

materials present at the toner surfaces as a quite small quantity, and the charge uniformity of the toner is promoted to suppress the roughening of images.

[0154]

5 As a result, even for a toner having a high circularity and a high chargeability, the excessive charge (charge-up phenomenon) in a long-term use can be alleviated if the exposed magnetic materials are present, so that Fe.iso (%) of at least 0.05 % is
10 important.

[0155]

For the above reason, Fe.iso (%) of 0.05 % - 3.00 % is necessary. Fe.iso (%) is preferably 0.05 - 2.00 %, more preferably 0.05 - 1.50 %, further
15 preferably 0.05 - 0.80 %.

[0156]

Also from the viewpoints of forming high-quality images through faithful reproduction of minute latent image dots in the present invention, the magnetic toner
20 weight-average particle size of 3 - 10 μm , particularly 4.0 - 8.0 μm , if preferred.

[0157]

A magnetic toner having a weight-average particle size (D4) below 3 μm is liable to cause a lower
25 transferability resulting in an increased amount of transfer residual toner which leads to difficulties such as toner melt-sticking and increased abrasion of

the image-bearing member in the contact charging section. Further, as the flowability and storability of the magnetic toner are lowered due to increased surface area of the entire magnetic toner, it becomes
5 difficult to uniformly charge the individual magnetic toner particles, thus resulting in image irregularities as by fog and lower transferability as well as abrasion and melt-sticking.

[0158]

10 If the magnetic toner has a weight-average particle size exceeding 10 μm , character or line images are liable to be accompanied with toner scattering, so that it becomes difficult to realize a high resolution. Further, in a high resolution image forming system, a
15 magnetic toner of $D_4 > 8 \mu\text{m}$ is liable to show a lower one-dot reproducibility.

[0159]

The particle size distributions and average particle sizes may be measured by using, e.g., Coulter
20 counter Model TA-II or Coulter Multicizer (respectively available from Coulter Electronics, Inc.). Herein, these values are determined based on values measured by using Coulter Multicizer connected to an interface (made by Nikkaki K.K.) and a personal computer
25 ("PC9801", made by NEC K.K.) for providing a number-basis distribution and a volume-basis distribution in the following manner. A 1 %-aqueous solution is

prepared as an electrolytic solution by using a reagent-grade sodium chloride (it is also possible to use ISOTON R-II (available from Coulter Scientific Japan K.K.)).

5 [0160]

For the measurement, 0.1 to 5 ml of a surfactant, preferably a solution of an alkylbenzenesulfonic acid salt, is added a dispersant onto 100 to 150 ml of the electrolytic solution, and 2 - 20 mg of a sample toner
10 is added thereto. The resultant dispersion of the sample in the electrolytic solution is subjected to a dispersion treatment for ca. 1 - 3 minutes by means of an ultrasonic disperser, and then subjected to measurement of particle size distribution in the range
15 of 2 μm or more by using the above-mentioned Coulter counter with a 100 μm -aperture to obtain a volume-basis distribution and a number-basis distribution.

[0161]

From the volume-basis distribution, a weight-average particle size (D_4) and a volume-average particle size (D_v) are calculated by using a central value as a representative value channel. From the number-basis distribution, and a number-average particle size (D_1) is calculated.

25 [0162]

The magnetic toner used in the present invention may preferably comprise toner particles produced

through the polymerization process. The toner according to the present invention can be produced through the pulverization process, but the toner particles produced through the pulverization process are generally indefinitely shaped and it is easy to obtain an average circularity of at least 0.920 as an essential requirement of the toner according to the present invention, but the toner particles have to be mechanically, thermally, or specially treated in order to have an average circularity of at least 0.950, or a preferable circularity of at least 0.970 (and also a preferred mode circularity of at least 0.990).

[0163]

Thus, in order to solve the above-mentioned various problems, in the present invention, the toner may preferably be produced through the polymerization process, examples of which may include: direct polymerization, suspension polymerization, emulsion polymerization, emulsion-association polymerization and seed polymerization. Among these, the suspension polymerization process is particularly preferred in order to easily provide a good balance of particle size and particle shape.

[0164]

In this suspension polymerization process for producing a toner according to the present invention, a monomeric mixture is formed by uniformly dissolving or

dispersing a monomer and coloring agent (and, optionally, other additives, such as wax, a colorant, a crosslinking agent and charge control agent), followed by melting and dispersing the monomeric mixture in a continuous layer (e.g., water phase) containing a dispersion stabilizer by means of an appropriate stirrer, and subjecting the dispersed monomeric mixture to suspension polymerization in the presence of a polymerization initiator to obtain toner particles of a desirable particle size.

[0165]

The polymerization toner polymerized through this suspension polymerization process (hereinafter referred to as "polymerization toner") is caused to comprise individual toner particles having a uniformly spherical shape, so that it is easy to obtain a toner having a circularity of at least 0.970 as a preferred physical requirement of the present invention, and further such a toner has a relatively uniform chargeability distribution, thus exhibiting a high transferability.

[0166]

However, by using a monomeric mixture containing ordinary magnetic powder at the time of suspension polymerization, it is difficult to suppress the exposure of the magnetic powder to the resultant toner particle surface, the resultant toner particles are liable to have remarkably lower flowability and

chargeability, and also it is difficult to obtain a toner having a desirable circularity because of strong interaction between the magnetic powder and water. This is (1) because magnetic powder particles are
5 generally hydrophilic, thus being liable to be localized at the toner particle surfaces, and (2) because at the time of suspension particles comprising monomer in a water solvent or at the time of stirring the suspension liquid during the polymerization, the
10 magnetic powder is moved at random within the suspended liquid droplets and the suspended liquid droplet surfaces comprising the monomer are pulled by the randomly moving magnetic powder, thereby distorting the liquid droplets from spheres. In order to solve such
15 problems, it is important to modify the surface property of the magnetic material particle.

[0167]

As for surface modification of magnetic powder to be used in a polymerization toner, many proposals have
20 been made. For example, JP-A 59-200254, JP-A 59-200256, JP-A 59-200257 and JP-A 59-224102 have proposed treatment of magnetic powder with various silane coupling agents, and JP-A 63-250660 has disclosed treatment of silicon-containing magnetic powder with
25 silane coupling agents.

[0168]

However, as a result of such a surface treatment,

the exposure of magnetic powder from the toner particle surfaces can be suppressed to some extent, but it is difficult to uniformly hydrophobize the magnetic powder surface, so that the occurrence of coalescent magnetic powder particles and yet-unhydrophobized magnetic powder particles is inevitable, and the suppression of the surface exposure of magnetic powder becomes insufficient.

[0169]

10 Further, JP-B 60-3181 has proposed a magnetic toner containing a magnetic iron oxide hydrophobized by treatment with an alkyltrialkoxysilane. The use of the thus-treated magnetic iron oxide powder has actually provided a toner having improved electrophotographic
15 performances in various aspects. However, the magnetic iron oxide powder inherently has a relatively low surface activity so that coalescence of magnetic powder particles and insufficient hydrophobization are inevitable, thus leaving the necessity of further
20 improvement for use in an image forming method operated under a severe condition as by inclusion of a contact charging step discussed hereinafter. The use of a large amount of hydrophobizing agent or a hydrophobizing agent having a higher viscosity provides
25 a higher hydrophobicity of the treated magnetic powder but also results in increased coalescence of magnetic powder particles, thus resulting in a rather inferior

dispersibility. As a result, a toner produced by using such a treated magnetic iron oxide powder is caused to have non-uniform triboelectric chargeability, leading to inferior fog prevention and transferability.

5 [0170]

As described above, a conventional polymerization toner using such a surface-treated magnetic powder has not succeeded in a good combination of hydrophobicity and dispersibility, and it is difficult to stably
10 obtain high-definition images if such a polymerization toner is used in an image forming method comprising a contact charging step as described hereinafter.

[0171]

As for magnetic powder used in the magnetic toner
15 of the present invention, it is extremely preferred that the magnetic materials are surface-treated for hydrophobization by dispersing magnetic iron oxide particles in an aqueous medium into primary particles thereof, and while maintaining the primary particle
20 dispersion state, hydrolyzing a coupling agent in the aqueous medium to surface-coat the magnetic iron oxide particles. According to this hydrophobization method in an aqueous medium, the magnetic iron oxide particles are less liable to coalesce with each other than in a
25 dry surface-treatment in a gaseous system, and the magnetic iron oxide particles can be surface-treated while maintaining the primary particle dispersion state

due to electrical repulsion between hydrophobized magnetic iron oxide.

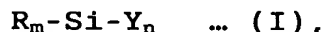
[0172]

The method of surface-treatment of magnetic iron oxide with a coupling agent while hydrolyzing the coupling agent in an aqueous medium does not require gas-generating coupling agents, such as chlorosilanes or silazanes, and allows the use of a high-viscosity coupling agent which has been difficult to use because of frequent coalescence of magnetic iron oxide particles in a conventional gaseous phase treatment, thus exhibiting a remarkable hydrophobization effect.

[0173]

As a coupling agent usable for surface-treating the magnetic iron oxide used in the present invention, a silane coupling agent or a titanate coupling agent may be used. A silicone coupling agent is preferred, and examples thereof may be represented by the following formula (I):

[Chemical Formula 1]



wherein R denotes an alkoxy group, Y denotes a hydrocarbon group, such as alkyl, vinyl, glycidoxy or methacryl, and m and n are respectively integers of 1 - 3 satisfying $m + n = 4$.

[0174]

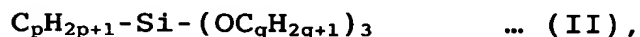
Examples of the silane coupling agents represented

by the formula (I) may include: vinyltrimethoxysilane, vinyltriethoxysilane, gamma-methacryloxypropyltrimethoxysilane, vinyltriacetoxysilane, methyltrimethoxysilane, methyltriethoxysilane, isobutyltrimethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, trimethylmethoxysilane, hydroxypropyltrimethoxysilane, phenyltrimethoxysilane, n-hexadecyltrimethoxysilane, and n-octadecyltrimethoxysilane.

10 [0175]

It is particularly preferred to use an alkyltrialkoxysilane coupling agent represented by the following formula (II) to treat the magnetic powder for hydrophobization in an aqueous medium:

15 [Chemical Formula 2]



wherein p is an integer of 2 - 20 and q is an integer of 1 - 3.

[0176]

20 In the above formula (II), if p is smaller than 2, the hydrophobization treatment may become easier, but it is difficult to impart a sufficient hydrophobicity, thus making it difficult to suppress the exposure of the magnetic powder to the toner particle surfaces. On the other hand, if p is larger than 20, the hydrophobization effect is sufficient, but the coalescence of the magnetic powder particles becomes

25

frequent, so that it becomes difficult to sufficiently disperse the treated magnetic powder particles in the toner, thus being liable to result in a toner exhibiting lower fog-prevention effect and transferability.

If q is larger than 3, the reactivity of the silane coupling agent is lowered, so that it becomes difficult to effect sufficient hydrophobization.

[0177]

It is particularly preferred to use an alkyltrialkoxysilane coupling agent represented by the formula (II) wherein p is an integer of 2 - 20 (more preferably an integer of 3 - 15), and q is an integer of 1 - 3 (more preferably an integer of 1 or 2).

The coupling agent may preferably be used in 0.05 - 20 wt. parts, more preferably 0.1 - 10 wt. parts, per 100 wt. parts of the magnetic powder.

[0178]

Herein, the term "aqueous medium" means a medium principally comprising water. More specifically, the aqueous medium includes water alone, and water containing a small amount of surfactant, a pH adjusting agent or/and an organic solvent. As the surfactant, it is preferred to use a nonionic surfactant, such as polyvinyl alcohol. The surfactant may preferably be added in 0.1 - 5 wt. parts per 100 wt. parts of water. The pH adjusting agent may include an inorganic acid,

such as hydrochloric acid. The organic solvent may include methanol which may preferably be added in a proportion of 0 - 500 wt. % of water.

[0179]

5 For the surface-treatment of magnetic iron oxide particles with a coupling agent in an aqueous medium, appropriate amounts of magnetic iron oxide particles and coupling agent may be stirred in an aqueous medium. It is preferred to effect the stirring by means of a
10 mixer having stirring blades, e.g., a high-shearing force mixer (such as an attritor or a TK homomixer) so as to disperse the magnetic iron oxide particles into primary particles in the aqueous medium under sufficient stirring.

15 [0180]

 The thus-surface treated magnetic iron oxide as free from particle agglomerates and individual particles are uniformly surface-hydrophobized. Accordingly, the magnetic powder is uniformly dispersed
20 in polymerization toner particles to provide almost spherical polymerization toner particles free from surface-exposure of the magnetic iron oxide. As a result, by using such magnetic iron oxide particles, it becomes possible to provide a toner having $Ca \geq 0.970$,
25 $C_{mod} \geq 0.990$ and $Fe_{iso} (\%) \leq 1.50 \%$.

 If such a magnetic toner is used in the image forming method of the present invention, the abrasion

of and toner melt-attachment onto the photosensitive member are further effectively suppressed, and it becomes possible to form high-quality images stably even in a low humidity environment.

5 [0181]

Further, while the magnetic toner has a uniformly high chargeability due to presence of no surface-exposed magnetic iron oxide, the magnetic toner of the present invention can provide good image during image
10 formation on a large number of sheets in a low temperature/low humidity environment due to the presence of electroconductive fine powder at the surfaces.

[0182]

15 It is preferred that the toner of the present invention contains a wax as described below in a proportion of 0.1 - 20 wt. % thereof.

[0183]

In the image forming method, a toner image
20 transferred onto a transfer(-receiving) material, such as paper, is thereafter fixed onto the transfer material by application of energy, such as heat and/or pressure, to provide a semipermanently image. In this instance, a hot roller-fixing scheme is frequently
25 adopted.

[0184]

By using a weight-average particle size of at most

10 μm , it is possible to obtain a very high-definition
image, but such a small-particle size toner particles
are liable to be buried between fibers of paper as a
typical transfer medium and fail to receive sufficient
5 heat, thus being liable to cause low-temperature
offset. However, by including an appropriate amount of
a wax as a release agent, the toner used in the present
invention can satisfy both a high resolution and anti-
offset characteristic as well as prevention of abrasion
10 of the photosensitive member.

[0185]

Examples of release agents usable in the toner
used in the present invention may include: petroleum
waxes and derivatives thereof, such as paraffin wax,
15 microcrystalline wax and petrolactum; montan wax and
derivatives thereof; hydrocarbon wax by Fischer-Tropsch
process and derivative thereof; polyolefin waxes as
represented by polyethylene wax and derivatives
thereof; and natural waxes, such as carnauba wax and
20 candelilla wax and derivatives thereof. The
derivatives may include oxides, block copolymers with
vinyl monomers, and graft-modified products. Further
examples may include: higher aliphatic alcohols, fatty
acids, such as stearic acid and palmitic acid, and
25 compounds of these, acid amide wax, ester wax, ketones,
hardened castor oil and derivatives thereof, vegetable
waxes and animal waxes.

[0186]

Among such waxes, it is preferred to use a wax showing a maximum heat-absorption peak in a temperature range of 40 - 110 °C, more preferably 45 - 90 °C, in
5 the course of temperature increase on a DSC cure measured by using a differential scanning calorimeter. The inclusion of a wax having maximum heat-absorption peak in the above-mentioned temperature range, contributes to improvements in low-temperature
10 fixability and effective releasability. If the maximum heat-absorption peak temperature (Tabs.max) is below 40 °C, the wax is liable to exhibit only a weak self-cohesion, thus lowering the anti-high-temperature offset characteristic. On the other hand, if Tabs.max
15 exceeds 110 °C, the fixation temperature is raised so that low-temperature offset is liable to occur. Further, in the case of production of toner by particle formation and polymerization in an aqueous medium, the wax is liable to precipitate during the particle
20 formation.

[0187]

The maximum heat-absorption peak temperature (Tabs.max) of a wax may be measured by using a differential scanning calorimeter (DSC) (e.g., "DSC-7",
25 available from Perkin-Elmer Corp.) according to ASTM D 3418-8. Temperature correction of the detector may be effected based on melting points of indium and zinc,

and calorie correction may be effected based on heat of fusion of indium. For the measurement, a sample is placed on an aluminum pan and subjected to heat at an increasing rate of 10 °C/min in parallel with a blank
5 aluminum pan as a control.

[0188]

The toner used in the present invention may preferably contain such a wax in a proportion of 0.1 - 20 wt. % of the entire toner. Below 0.1 wt. %, the
10 low-temperature offset-suppression effect is poor, and above 20 wt. %, the long-term storability is lowered and the dispersibility of the other toner ingredients becomes lowered to result in lower flowability and image forming performances of the resultant toner.

15 [0189]

The toner used related to the present invention can further contain a charge control agent so as to stabilize the chargeability. Known charge control agents can be used. It is preferred to use a charge
20 control agent providing a quick charging speed and stably providing a constant charge. In the case of polymerization toner production, it is particularly preferred to use a charge control agent showing low polymerization inhibition effect and substantially no
25 solubility in aqueous dispersion medium.

[0190]

Specific examples of negative charge control

agents may include: metal compounds of aromatic carboxylic acids, such as salicylic acid, alkylsalicylic acids, dialkylsalicylic acids, naphthoic acid, and dicarboxylic acids; metal salts or metal
5 complexes of azo-dyes and azo pigments; polymeric compounds having a sulfonic acid group or carboxylic acid group in side chains; boron compounds, urea compounds, silicon compounds, and calixarenes.
[0191]

10 Positive charge control agents may include: quaternary ammonium salts, polymeric compounds having such quaternary ammonium salts in side chains, quinacridone compounds, nigrosine compounds and imidazole compounds.

15 [0192]

The charge control agent may be included in the toner by internal addition or external addition to the toner particles. The amount of the charge control agent can vary depending on toner production process
20 factors, such as binder resin species, other additives and dispersion methods, but may preferably be 0.1 - 10 wt. parts, more preferably 0.1 - 5 wt. parts, per 100 wt. parts of the binder resin.
[0193]

25 In the case of providing a negative toner, it is preferred to add a metal salt or a metal complex of an azo dye or an azo pigment.

However, it is not essential for the toner related to the present invention to contain a charge control agent, but the toner need not necessarily contain a charge control agent by positively utilizing the
5 triboelectrification with a toner layer thickness-regulating member and a toner-carrying member.

[0194]

Next, description will be made on the magnetic iron oxide and the binder resin contained in the
10 magnetic toner of the present invention.

The magnetic toner particles of the present invention contain at least a magnetic iron oxide, such as magnetite, maghemite, or ferrite.

[0195]

15 Magnetic iron oxide to be contained in the toner base particles to make the toner magnetic toner in the present invention may include: magnetic iron oxide, such as magnetite, maghemite, or ferrite; metals, such as iron, cobalt, or nickel, or alloys or mixtures of
20 these metals with aluminum, cobalt, copper, lead, magnesium, tin, zinc, antimony, beryllium, bismuth, cadmium, calcium, manganese, selenium, titanium, tungsten, and vanadium.

[0196]

25 The magnetic iron oxide may preferably have a BET specific surface area (S_{BET}) of 2 - 30 m^2/g , more preferably 3 - 28 m^2/g , as measured according to

nitrogen-absorption, and a Mohs' hardness of 5 - 7.

[0197]

For providing the magnetic toner used in the present invention, the magnetic iron oxide may preferably be used in 10 - 200 wt. parts, more preferably 20 - 180 wt. parts, per 100 wt. parts of the binder resin. Below 10 wt. parts, the coloring power of the resultant toner is liable to be insufficient, and the suppression of fog becomes difficult. Above 200 wt. parts, the resultant toner is held at an excessively large force onto the toner-carrying member, to show a lower developing performance. Moreover, the dispersion of magnetic iron oxide to individual toner particles becomes difficult, and the fixability is lowered.

[0198]

The magnetic iron oxide related to the constitution of the magnetic toner used in the image forming method of the invention may be produced, e.g., in the following manner, in the case of magnetite-based magnetic iron oxide.

[0199]

To a ferrous salt aqueous solution, an alkali, such as sodium hydroxide, in an amount equivalent to the iron in the ferrous salt or larger to prepare an aqueous solution containing ferrous hydroxide. While retaining the pH of the thus-prepared aqueous solution

at pH 7, preferably pH 8 - 10 and warming the aqueous solution at a temperature of 70 °C or higher, air is blown into the aqueous solution to oxidize the ferrous hydroxide, thereby first forming seed crystals
5 functioning as nuclei of magnetic iron oxide particles to be produced.

[0200]

Then, to the slurry-form liquid containing the seed crystals, an aqueous solution containing ferrous
10 salt in an amount of ca. 1 equivalent based on the amount of the previously added alkali, is added. While keeping the liquid at pH 6 - 10, air is blown thereinto to proceed with the reaction of the ferrous hydroxide, thereby growing magnetic iron oxide particles around
15 the seed crystals as nuclei. Along with the progress of the oxidation reaction, the liquid pH is shifted toward an acidic side, but is preferred not to allow the liquid pH go down to below 6. At a final stage of the oxidation, the liquid pH is adjusted, and the
20 slurry liquid is sufficiently stirred so as to disperse the magnetic iron oxide in primary particles. In this state, a coupling agent for hydrophobization is added to the liquid to be sufficiently mixed under stirring. Thereafter, the slurry is filtered out and dried, and
25 the dried product is lightly disintegrated to provide hydrophobic treated magnetic iron oxide particles.

[0201]

Alternatively, the iron oxide particles after the oxidation reaction may be washed, filtered out and then, without being dried, re-dispersed in another aqueous medium. Then, the pH of the redispersion liquid is adjusted and subjected to hydrophobization by adding a coupling agent under sufficient stirring. Anyway, it is vital that untreated iron oxide particles formed in the oxidation reaction system are subjected to hydrophobization in their wet slurry state and without being dried prior to the hydrophobization.

[0202]

As the ferrous salt used in the above-mentioned production process, it is generally possible to use ferrous sulfate by-produced in the sulfuric acid process for titanium production or ferrous sulfate by-produced during surface washing of steel sheets. It is also possible to use ferrous chloride. In the above-mentioned process for producing magnetic iron oxide from a ferrous salt aqueous solution, a ferrous salt concentration of 0.5 - 2 mol/liter is generally used so as to obviate an excessive viscosity increase accompanying the reaction and in view of the solubility of a ferrous salt, particularly of ferrous sulfate. A lower ferrous salt concentration generally tends to provide finer magnetic iron oxide particles. Further, as for the reaction conditions, a higher rate of air supply, and a lower reaction temperature, tends to

provide a finer product particles.

[0203]

By using magnetic toner containing the thus-produced hydrophobic magnetic iron oxide particles, it
5 becomes possible to realize an image forming method wherein the abrasion of an toner attachment onto the photosensitive member are effectively suppressed to stably provide high-quality images.

[0204]

10 The magnetic iron oxide may have octahedral, hexahedral, spherical, acicular or flaky shape, but magnetic iron oxide particles having less anisotropic shapes, such as octahedral, hexahedral or spherical are preferred in order to provide a high image density.
15 Such shapes may be confirmed by observation through a scanning electron microscope (SEM).

[0205]

It is preferred that the magnetic iron oxide have a volume-average particle size of 0.1 - 0.3 μm and
20 contain at most 40 % by number of particles of 0.03 - 0.1 μm , based on measurement of particles having particle sizes of at least 0.03 μm . It is further preferred that the amount of particles of 0.3 μm or larger is suppressed to at most 10 % by number.

25 [0206]

Magnetic materials having an average particle size of below 0.1 μm are not generally preferred because

they are liable to provide a magnetic toner giving images which are somewhat tinted in red and insufficient in blackness with enhanced reddish tint in halftone images, thus not suitable for generally speaking. Further, as the magnetic materials are caused to have an increased surface area, the dispersibility thereof is lowered, and an inefficiently larger energy is consumed for the production. Further, the coloring power of the added magnetic materials can be lowered to result in insufficient image density in some cases.

[0207]

On the other hand, if the magnetic materials have an average particle size in excess of 0.3 μm , the weight per one particle is increased to increase the probability of exposure thereof to the toner particle surface due to a specific gravity difference with the binder during the production. Further, the wearing of the production apparatus can be substantially promoted and the settling stability of a dispersed substances is liable to become unstable, thus not preferable.

[0208]

Further, if particles of 0.1 μm or smaller exceed 40 % by number of total particles, the magnetic materials are liable to have a lower dispersibility because of an increased surface area, liable to form agglomerates in the toner to impair the toner

chargeability, and are liable to have a lower coloring power.

If the percentage is lowered to at most 30 % by number, the difficulties are preferably alleviated.

5 [0209]

Incidentally, magnetic iron oxide having particle sizes of below 0.03 μm receive little stress during the toner production so that the probability of exposure thereof to the toner particle surface is low. Further, even if such minute particles are exposed to the toner particle surface, they do not substantially function as leakage sites lowering the chargeability of the toner particles. Accordingly, the particles of 0.03 - 0.1 μm are noted herein, and the percentage by number thereof is suppressed to below a certain limit. On the other hand, if particles of 0.3 μm or larger exceed 10 % by number, the magnetic iron oxide particles are caused to have a lower coloring power, thus being liable to result in a lower image density. Further, as the number of magnetic iron oxide particles is decreased at an identical weight percentage, it becomes difficult statistically to have the magnetic iron oxide particles be present up to the proximity of the toner particle surface and distribute equal numbers of magnetic materials to respective toner particles. This is undesirable. It is further preferred that the percentage be suppressed to at most 5 % by number.

[0210]

In the present invention, it is preferred that the magnetic iron oxide production conditions are adjusted so as to satisfy the above-mentioned conditions for the particles size distribution, or the produced magnetic iron oxide is used for the toner production after adjusting the particle size distribution as by pulverization and/or classification. The classification may suitably be performed by utilizing sedimentation as by a centrifuge or a thickener, or wet classification using, e.g., a cyclone.

[0211]

The volume-average particle size and particle size distribution of iron oxide particles described herein are based on values measured in the following manner.

Sample particles in a sufficiently dispersed state are photographed at a magnification of 3×10^4 through a transmission electron microscope (TEM), and 100 particles each having a particle size of at least 0.03 μm selected at random in visual fields of the taken photographs are subjected to measurement of projection areas. The particle size (projection area-equivalent circle diameter (D_{CE})) of each particle is determined as a diameter of a circle having an area equal to the measured projection area of the particle. Based on the measured particle sizes of the 100 particles, a volume-average particle size ($D_v = \sqrt[3]{\sum n D_{CE}^3 / \sum n}$), percentage

by number of particles of $0.03\ \mu\text{m}$ - $0.1\ \mu\text{m}$ and percentage by number of particles of $0.3\ \mu\text{m}$ or larger are determined.

[0212]

- 5 The volume-average particle size and particle size distribution of magnetic iron oxide dispersed within toner particles may be measured in the following manner.

Sample toner particles are sufficiently dispersed
10 in a cold-setting epoxy resin, which is then hardened for 2 days at $40\ ^\circ\text{C}$. The hardened product is sliced into thin flakes by a microtome. The thin flakes are observed through a TEM and photographic at magnification of 1×10^4 - 4×10^4 . One hundred iron oxide
15 particles of at least $0.03\ \mu\text{m}$ in particle size selected at random in visual fields of the taken photographs are subjected to measurement of projection areas. From the projection areas of the 100 iron oxide particles, a volume-average particle size (projection area-
20 equivalent circular diameter), percentage by number of particles of $0.03\ \mu\text{m}$ - $0.1\ \mu\text{m}$ and percentage by number of particles $0.3\ \mu\text{m}$ or larger are determined similarly as the above.

[0213]

- 25 The magnetic iron oxide may preferably have magnetic properties including a saturation magnetization of 10 - $200\ \text{Am}^2/\text{kg}$ as measured at a

magnetic field of 795.8 kA/m, a residual magnetization of 1 - 100 Am²/kg, and a coercive force of 1 - 30 kA/m. These types of magnetic iron oxide are used at 20 - 200 wt. parts with binder resin of 100 wt. parts. Among
5 these types of magnetic iron oxide, that of using magnetite as a main component is especially preferable.
[0214]

It is particularly preferred that the magnetic toner used in the present invention has a magnetization
10 of 10 - 50 Am²/kg at a magnetic field of 79.6 kA/m (1000 oersted).
[0215]

The magnetization at a magnetic field of 79.6 mA/m is taken as a property of a magnetic toner in a
15 magnetic field realized in an actual image forming apparatus, while the saturation magnetization is used as a parameter representing magnetic properties of magnetic iron oxide. The magnetic field acting on magnetic toners is most commercially available image
20 forming apparatus is on the order of several tens to a hundred and several tens kA/m so as to avoid the leakage of excessively large magnetic field to outside the image forming apparatus and suppress the cost of the magnetic field supply. Accordingly, a magnetic field
25 of 79.6 kA/m (1000 oersted) is taken as a representative magnetic field value actually acting on a magnetic toner in image forming apparatus to define a

magnetization of a magnetic toner.

[0216]

A magnetic toner is held within a developing device without causing toner leakage by disposing a magnetic force generating means in the developing
5 device. The conveyance and stirring of the magnetic toner is also effected under a magnetic force. By disposing a magnetic force generating means so that the magnetic force acts on the toner-carrying member, the
10 recover of transfer residual toner is further promoted in the simultaneous developing and toner recovery system and toner scattering is prevented by forming ears of magnetic toner on the toner-carrying member.

[0217]

15 However, if the toner has a magnetization of below $10 \text{ Am}^2/\text{kg}$ at a magnetic field of 79.6 kA/m , it becomes difficult to convey the toner on the toner-carrying member, and toner ear formation on the toner-carrying member becomes unstable, thus failing to provide
20 uniform charge to the toner. As a result, image defects, such as fog, image density irregularity and recovery failure of transfer-residual toner are liable to be caused. If the magnetization exceeds $50 \text{ Am}^2/\text{kg}$, the toner particles are liable to have an increased
25 magnetic agglomeratability, to result in remarkably lower flowability and transferability. As a result, the transfer-residual toner is increased. Further, if

the amount of magnetic iron oxide is increased in order to enhance the magnetization, the resultant toner is caused to have a lower fixability.

[0218]

5 The magnetic values described herein are based on values measured at 25 °C under an external magnetic field of 79.6 kA/m for magnetization of magnetic toners and at 25 °C under an external magnetic field of 796 kA/m for magnetic properties of magnetic iron oxides, 10 respectively by using an oscillation-type magnetometer ("VSM P-1-10, made by Toei Kogyo K.K.).

[0219]

 The magnetic toner used in the present invention can further contain another colorant in addition to the 15 magnetic iron oxide. Examples of such another colorant may include: magnetic or non-magnetic inorganic compounds, and known dyes and pigments. Specific examples thereof may include: particles of ferroelectric metals, such as cobalt, nickel and iron, 20 alloys of these with chromium, manganese, copper, zinc, aluminum and rare earth elements; hematite, titanium black, nigrosine dyes/pigments, carbon black and phthalocyanine. The materials may also be surface-treated similarly as the magnetic iron oxide.

25 [0220]

 Next, the suspension polymerization process will be described as a process for producing the magnetic

toner particles used in the present invention.

[0221]

Examples of polymerizable monomers for constituting the binder resin in the magnetic iron oxides may include: styrene monomers, such as styrene, 5 o-methylstyrene, m-methylstyrene, p-methylstyrene, p-methoxystyrene and p-ethylstyrene; acrylate esters, such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, n-propyl acrylate, n-octyl 10 acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, stearyl acrylate, 2-chloroethyl acrylate and phenyl acrylate; methacrylate esters, such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, isobutyl 15 methacrylate, n-octyl methacrylate, dodecyl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, phenyl methacrylate, dimethylaminoethyl methacrylate, and diethylaminoethyl methacrylate; and other acrylonitrile, methacrylonitrile and acrylamide.

20 [0222]

These monomers may be used singly or in mixture. Among these, styrene or a styrene derivative may preferably be used singly or in mixture with another monomer so as to provide a toner with good developing 25 performances and continuous image forming performances.

[0223]

In the polymerization toner production according

to the present invention, it is possible to add a resin into the monomer to be polymerized. For example, if it is described to introduce a hydrophilic functional group, such as amino group, hydroxyl group, sulfonic acid group, glycidyl group or nitrile group, into toner particles, while such a monomer containing such a hydrophilic group cannot be used because of its water-solubility to be emulsified in an aqueous medium, it is possible to incorporate a random copolymer, a block copolymer or a graft copolymer of such a monomer with another vinyl monomer, such as styrene or ethylene. It is also possible to incorporate a polycondensate, such as a polyester or a polyamide, or an addition polymer, such as a polyether or a polyimine.

15 [0224]

If such a polymer having a polar functional group is contained in toner, the above-mentioned wax can be effectively enclosed therein by phase separation to provide a toner with a good combination of anti-offset property, anti-blocking property and low-temperature fixability.

[0225]

Such a polymer having a polar functional group, when used, may preferably have a average weight of 5000 or below. If the molecular weight is below 5000, particularly 4000 or below, the polymer is concentrated at proximity to the surfaces, to result in negative

influence on developing performance and anti-blocking property, thus not preferable.

[0226]

Further, for the purpose of improving the

5 dispersibility of ingredients and the fixability and image forming performance of the resultant toner, it is possible to add a resin other than the above in the monomers. Examples of such another resin may include: homopolymers of styrene and its substituted

10 derivatives, such as polystyrene and polyvinyltoluene; styrene copolymers, such as styrene-popylene copolymer, styrene-vinyltoluene copolymer, styrene-vinylnaphthalene copolymer, styrene-methyl acrylate copolymer, styrene-ethyl acrylate copolymer, styrene-

15 butyl acrylate copolymer, styrene-octyl acrylate copolymer, styrene-dimethylaminoethyl acrylate copolymer, styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-butyl methacrylate copolymer, styrene-dimethylaminoethyl

20 methacrylate copolymer, styrene-vinyl methyl ether copolymer, styrene-vinyl ethyl ether copolymer, styrene-vinyl methyl ketone copolymer, styrene-butadiene copolymer, styrene-isoprene copolymer, styrene-maleic acid copolymer, and styrene-maleic acid

25 ester copolymers; polymethyl methacrylate, polybutyl methacrylate, polyvinyl acetate, polyethylene, polypropylene, polyvinyl butyral, silicone resin,

polyester resin, polyamide resin, epoxy resin, polyacrylic acid resin, rosin, modified rosin, terpene resin, phenolic resin, aliphatic or alicyclic hydrocarbon resins, and aromatic petroleum resin.

- 5 These resins may be used singly or in combination of two or more species.

[0227]

- Such a resin may preferably be added in 1 - 20 wt. parts per 100 wt. parts of the monomer. Below 1 wt. part, the addition effect thereof is scarce, and above 20 wt. parts, the designing of various properties of the resultant polymerization toner becomes difficult.
- 10

[0228]

- Further, if a polymer having a molecular weight which is different from that of the polymer obtained by the polymerization is dissolved in the monomer for polymerization, it is possible to obtain a toner having a broad molecular weight distribution and thus showing a high anti-offset property.
- 15

20 [0229]

- A polymerization initiator to be used in the production of the polymerization toner according to the present invention, exhibiting a halflife of 0.5 - 30 hours at the polymerization temperature may be added in an amount of 0.5 - 29 wt. % of the polymerizable monomer so as to obtain a polymer exhibiting a maximum in a molecular weight range of 1×10^4 - 1×10^5 , thereby
- 25

providing the toner with a desirable strength and appropriate melt-characteristics.

[0230]

Examples of the polymerization initiator may include: azo- or diazo-type polymerization initiators, such as 2,2'-azobis-(2,4-dimethylvaleronitrile), 2,2'-azobisisobutyro-nitrile, 1,1'-azobis(cyclohexane-2-carbonitrile), 2,2'-azobis-4-methoxy-2,4-dimethylvaleronitrile, azobisisobutyronitrile; and peroxide-type polymerization initiators such as benzoyl peroxide, methyl ethyl ketone peroxide, diisopropyl peroxy-carbonate, cumene hydroperoxide, 2,4-dichlorobenzoyl peroxide, lauroyl peroxide, and t-butyl peroxy-2-ethylhexanoate.

15 [0231]

The polymerizable monomer composition for preparing polymerization toner according to the present invention can further contain a crosslinking agent in a proportion of preferably 0.001 - 15 wt.%.

20 The crosslinking agent may for example be a compound having two or more polymerizable double bonds. Examples thereof may include: aromatic divinyl compounds, such as divinylbenzene, and divinyl naphthalene; carboxylate esters having two double bonds, such as ethylene glycol diacrylate, 25 ethylene glycol dimethacrylate, and 1,3-butane diol dimethacrylate; divinyl compounds, such as

divinylaniline, divinyl ether, divinyl sulfide and
vidinyl sulfone; and compounds having three or more
vinyl groups. These may be used singly or in mixture.
[0232]

5 In order to produce the toner through a suspension
polymerization process of the present invention, the
above-mentioned toner mixture, i.e., a mixture of a
polymerizable monomer and magnetic powder, and other
toner components a wax, plasticizer, a charge control
10 agent, a crosslinking agent, and a colorant, as
desired; further optional ingredients, such as an
organic solvent polymer, an additive polymer, and
dispersing agent, subjected to uniform dissolution or
dispersion by a dispersing machine, such as a
15 homogenizer, a ball mill, a colloid mill, a developer,
or an ultrasonic dispersing machine, may be suspended
in an aqueous medium.

[0233]

 At this time, it is preferred to use a high-speed
20 dispersing machine, such as a high-speed stirrer or an
ultrasonic dispersing machine to form droplets of the
monomeric mixture in desired size at a stroke in order
to provide toner particles of a narrower particle size
distribution. The polymerization initiator may be
25 added to the polymerization system by adding it to the
monomeric mixture together with the other ingredients
for providing the monomeric mixture or just before

dispersing the monomeric mixture in the aqueous medium. Alternatively, it is also possible to add such peroxide polymerization initiator in solution within a polymerizable monomer or another solvent into the
5 polymerization system just after the formation of the droplets of the monomeric mixture and before the initiation of the polymerization.

[0234]

After the formation of the droplets, the method
10 may be stirred by an ordinary stirrer at an appropriate degree for maintaining droplets state and preventing the floating or sedimentation of the droplets.

[0235]

Into the suspension polymerization method
15 according to the present invention, a dispersion stabilizer may be added. As the dispersion stabilizer, it is possible to use a know surfactant or organic or inorganic dispersion agent. Among these, an inorganic dispersing agent may be preferably be used because it
20 is less liable to result in excessively small particles which can cause some image defects, its dispersion function is less liable to be impaired even at a temperature change because its stabilizing function principally relies on its stearic hindrance, and also
25 it can be readily removed by washing to be less liable to adversely affect the resultant toner performance.

[0236]

Examples of such an inorganic dispersing agent may include: polyvalent metal phosphates, such as calcium phosphate, magnesium phosphate, aluminum phosphate, and zinc phosphate; carbonates, such as calcium carbonate
5 and magnesium carbonate; inorganic salts, such as calcium metasilicate, calcium sulfate, and barium sulfate; and inorganic oxides, such as calcium hydroxide, magnesium hydroxide, aluminum hydroxide, silica bentonite, and alumina.

10 [0237]

Such an inorganic dispersing agent may desirably be used singly in an amount of 0.2 - 20 wt. parts per 100 wt. parts of the polymerizable monomeric mixture, but it is also possible to use 0.001 - 0.1 wt. part of
15 a surfactant in combination particularly for preparation of toner particles having an average particle size of at most 5 μm .

[0238]

Examples of such a surfactant may include: sodium
20 dodecylbenzenesulfate, sodium tetradecylsulfate, sodium tetradecylsulfate, sodium pentadecylsulfate, sodium octylsulfate, sodium oleate, sodium laurate, sodium stearate, and potassium stearate.

[0239]

25 An inorganic agent as mentioned above may be used as it is but may be produced in situ in the aqueous medium for suspension polymerization in order to

provide toner particles of a narrower particle size distribution. For example, in the case of calcium phosphate, a sodium phosphate aqueous solution and a calcium phosphate aqueous solution may be blended under
5 high-speed stirring to form water-insoluble calcium phosphate, which allows the dispersion of a monomeric mixture into droplets of a more uniform size. At this time, water-soluble sodium chloride is by-produced, but the presence of such a water-soluble salt is effective
10 for suppressing the dissolution of a polymerizable monomer into the aqueous medium, thus conveniently suppressing the formation of ultrafine toner particles owing to emulsion polymerization.

[0240]

15 The remaining of such a salt can adversely affect the removal of residual monomer after the polymerization so that it is preferred to replace the aqueous medium or effect desalting by using an iron-exchange resin. The inorganic dispersing agent can be
20 substantially completely removed by washing with acid or alkali after the polymerization.

[0241]

The temperature for the suspension polymerization may be set to at least 40 °C, generally in a range of
25 50 - 90 °C. The polymerization in this temperature range is preferred because the releasing agent and waxes are precipitated by phase separation to be

enclosed more completely. In order to consume the residual polymerization monomer, the temperature can be raised up to 90 - 150 °C in the final stage of the polymerization.

5 [0242]

The polymerization toner particles after the polymerization may be recovered by filtration, washing and drying, and then blended with inorganic fine powder and electroconductive fine powder for attachment onto
10 the surfaces. It is also a preferred mode to include a step for classifying the polymerization toner particles to remove a coarse and/or a fine powder fraction.

[0243]

Then, a pulverization process as another process
15 for producing the magnetic toner particles used in the present invention, will be described.

[0244]

The production of toner according to the present invention through the pulverization process may be
20 performed in a known manner. For example, toner ingredients, inclusive of the binder resin, magnetic iron oxide, a release agent, a charge control agent, and optionally another colorant, etc., are sufficiently blended by a blender, such as a Henschel mixer or a
25 ball mill, and then melt-kneaded by a hot kneading means, such as a hot roller, a kneader or an extruder, to form a molten mixture of resinous materials and

dispenser therein other powdery toner materials such as magnetic iron oxide particles. The melt-kneaded product, after being cooled for solidification, is pulverized, classified and optionally surface-treated to obtain magnetic toner particles, which are then blended with the fine powder to obtain a magnetic toner related to the present invention. Either the classification or the surface treatment can be performed in advance. In the classification, it is preferred to use a multi-division classifier in view of the production efficiency.

[0245]

The pulverization may be performed by using a known pulverization apparatus of, e.g., the mechanical impact type or the jet type. In order to obtain a toner having the specified circularity according to the present invention, it is preferred to effect the pulverization under heating or apply a supplemental mechanical impact. It is also possible to subject the pulverized (and optionally classified) toner particles to dispersion into hot water or passing through hot air stream.

[0246]

Examples of the mechanical impact application apparatus may include: mechanical impacting pulverizers, such as "Krypron System" (made by Kawasaki Jukogyo K.K.) and "Trubomill" (made by Turbo Kogyo

K.K.), and mechanical impacting devices, such as "Mechanofusion System" (made by Hosokawa Micron K.K.) and "Hybridization System" (made by Nara Kikai Seisakusho K.K.) wherein toner particles are pressed
5 against in inner wall of a casing under action of a centrifugal force exerted by blades stirring at high speeds, thereby applying mechanical impact forces including compression and abrasion forces to the toner particles.

10 [0247]

For the mechanical impact application treatment for sphering of toner, it is preferred that the treatment atmosphere temperature is selected in a range of temperature $T_g \pm 10$ °C around the glass transition
15 temperature (T_g) of the toner, in view of agglomeration prevention and productivity. A treatment temperature in a range of $T_g \pm 5$ °C is further preferred for providing an improved transferability.

[0248]

20 The toner according to the present invention can be produced by a method described in JP-A 56-13945 and the others that a melted mixture is atomized into air using a disk or a multi-fluid nozzle to obtain a spherical toner, a dispersed polymerization method
25 which directly generates a toner using a aqueous organic solvent which is soluble in a monomer and resultant-polymer is insoluble, or an emulsifying

polymerization method represented by a soap-free polymerization which generates a toner through direct polymerization under the condition where water-soluble polar polymerization initiator presents.

5 [0249]

Examples of the binder resin for producing the magnetic toner particles of the present invention through the pulverization process may include: homopolymers of styrene and its substituted derivatives,
10 such as polystyrene and polyvinyltoluene; styrene copolymers, such as styrene-propylene copolymer, styrene-vinyltoluene copolymer, styrene-vinylnaphthalene copolymer, styrene-methyl acrylate copolymer, styrene-ethyl acrylate copolymer, styrene-
15 butyl acrylate copolymer, styrene-octyl acrylate copolymer, styrene-dimethylaminoethyl acrylate copolymer, styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-butyl methacrylate copolymer, styrene-dimethylaminoethyl
20 methacrylate copolymer, styrene-vinyl methyl ether copolymer, styrene-vinyl ethyl ether copolymer, styrene-vinyl methyl ketone copolymer, styrene-butadiene copolymer, styrene-isoprene copolymer, styrene-maleic acid copolymer, and styrene-maleic acid
25 ester copolymers; polymethyl methacrylate, polybutyl methacrylate, polyvinyl acetate, polyethylene, polypropylene, polyvinyl butyral, silicone resin,

polyester resin, polyamide resin, epoxy resin,
polyacrylic acid resin, rosin, modified rosin, terpene
resin, phenolic resin, aliphatic or alicyclic hydrocarbon
resins, aromatic petroleum resin, paraffin wax, and
5 carnauba wax . These resins may be used singly or in
combination of two or more species. It is particularly
preferred to use a styrene copolymer and/or a polyester
resin in view of the developing performance and the
fixability.

10 [0250]

The binder resin may preferably have a glass
transition temperature (T_g) of 50 - 70 °C. Below 50
°C, the resultant magnetic toner is liable to have a
lower storability, and above 70 °C, the fixability
15 tends to be lowered.

[0251]

Next, the inorganic fine powder and the
electroconductive fine powder contained in the magnetic
toner of the present invention will be described.

20 [0252]

The magnetic toner of the present invention
contains inorganic fine powder, preferably having an
average primary particle size of 4 - 80 nm, as a
flowability improving agent. The inorganic fine powder
25 may be added to provide the magnetic toner with an
improved flowability and uniformize the chargeability
of the magnetic toner particles, and for this purpose,

it is preferred to subject the inorganic fine powder to hydrophobization thereby adjusting the chargeability and improve the environmental stability of the magnetic toner.

5 [0253]

In case where the inorganic fine powder has a number-average primary particle size larger than the 80 nm or the inorganic fine powder is not added, the transfer-residual toner particles, when attached to the charging member, are liable to stick to the charging member, so that it becomes difficult to stably attain good uniform chargeability of the image-bearing member. Further, it becomes difficult to have a sufficient flowability of the toner, thus being liable to cause difficulties, such as non-uniform charges to the toner particles, increased fog, image density lowering and toner scattering.

[0254]

In case where the inorganic fine powder has a number-average primary particle size below 4 nm, the inorganic fine powder is caused to have strong agglomeratability, not primary particle, so that the inorganic fine powder is liable to have a broad particle size distribution including agglomerates of which the disintegration is difficult, rather than the primary particles, thus being liable to result in image defects such as image dropout due development with the

agglomerates of the inorganic fine powder and defects attributable to damages on the image-bearing member, developer-carrying member of contact charging member, by the agglomerates. For providing a more uniform
5 charge distribution of the toner particles, it is further preferred that the number-average primary particle size of the inorganic fine powder is in the range of 6 - 35 nm.

[0255]

10 The number-average primary particle size of inorganic fine powder described herein is based on the values measured in the following manner. A toner sample is photographed in an enlarged form through a scanning electron microscope (SEM) equipped with an
15 elementary analyzer as XMA to provide an ordinary SEM picture and also an XMA picture mapped with elements contained in the inorganic fine powder. Then, by comparing these pictures, the sizes of 100 or more inorganic fine powder primary particles attached onto
20 the toner surface or isolated from the toner particles are measured to provide a number-average particle size.

[0256]

The inorganic fine powder used in the present invention may preferably comprise fine powder of at
25 least one species selected from the group consisting of silica, titania and alumina.

[0257]

For example, hydrated silica fine powder may be dry-process silica (sometimes called fumed silica) formed by vapor phase oxidation of a silicon halide or so-called wet process silica formed from water glass.

5 However, dry process silica is preferred because of fewer silanol groups at the surface and inside thereof and also fewer production residues such as Na_2O and SO_3^{2-} . The dry process silica can be in the form of and include complex metal oxide powder with other metal
10 oxides for example by using another metal halide, such as aluminum chloride or titanium chloride together with silicon halide in the production process.

[0258]

The inorganic fine powder may preferably be added
15 in a proportion of 0.1 - 3.0 wt. % of the magnetic toner particles. Below 0.1 wt. %, the addition effect thereof is scarce, and above 30 wt. %, the fixability of the toner is lowered.

[0259]

20 The inorganic fine powder used in the present invention may preferably have been hydrophobized in view of performances in a high temperature/high humidity environment. If the inorganic fine powder added to the toner absorbs mixture, the chargeability
25 of the toner particles is remarkably lowered, thus being liable to cause toner scattering.

[0260]

As the hydrophobization agents, it is possible to use silicone varnish, various modified silicone varnish, silicone oil, various modified silicone oil, silane compounds, silane coupling agents, other organic
5 silicon compounds and organic titanate compounds singly or in combination.

[0261]

Among these, it preferred that the inorganic fine powder has been treated with at least silicone oil,
10 more preferably treated with silicone oil simultaneously with or after hydrophobization treatment with a silane coupling agent, in order to keep a high chargeability of the magnetic toner particles to prevent toner scattering, even in a high humidity
15 environment.

[0262]

In such a preferred form of the treatment of the inorganic fine powder, silylation is performed in a first step to remove a hydrophilic site, such as a
20 silanol group of silica, by a chemical bonding, and then a hydrophobic film is formed of silicone oil in a second step.

[0263]

The silicone oil may preferably have a viscosity
25 at 25 °C of 10 - 200,000 mm²/s, more preferably 3,000 - 80,000 mm²/s. If the viscosity is below 10 mm²/sec, the treated inorganic fine powder is liable to lack

stability and result in image deterioration due to thermal or mechanical shock. On the other hand, if the viscosity is larger than 200,000 mm²/sec, the treatment of the inorganic fine powder with the silicone oil is
5 liable to become difficult.

[0264]

Particularly preferred species of the silicone oil used may include: dimethylsilicone oil, methylphenylsilicone oil, α -methylstyrene-modified
10 silicone oil, chlorophenylsilicone oil, and fluorine-containing silicone oil.

[0265]

The silicone oil treatment may be performed, e.g., by directly blending the inorganic fine powder
15 (optionally preliminarily treated with e.g., silane coupling agent) with silicone oil by means of a blender such as a Henschel mixer; and by spraying silicone oil onto the inorganic fine powder.

[0266]

20 Or the silicone oil treatment may be performed by dissolving or dispersing silicone oil in an appropriate solvent and adding thereto the inorganic fine powder for blending, followed by removal of the solvent. In view of less by-production of the agglomerates, the
25 spraying is particularly preferred.

[0267]

The amount of silicon oil treatment is preferably

1 - 23 wt. parts per 100 wt. parts of inorganic fine powder, and more preferably 5 - 20 wt. parts. If the amount of silicon oil is too small, good hydrophobicity cannot be obtained and if it is too much, defects such as fob may be caused.

[0268]

The inorganic fine powder having a number-average primary particle size of 4 - 80 nm may preferably have a specific surface area of 20 - 250 m²/g, more preferably 40 - 200 m²/g; as measured by the nitrogen adsorption BET method.

[0269]

The specific surface area was calculated by the BET multi-point method using a specific surface area meter ("Autosorb 1", made by Yuasa Ionix K.K.).

[0270]

The toner of the present invention contains electroconductive fine powder as described below.

Electroconductive fine powder may preferably be contained in 0.2 - 10 wt. % of the entire toner. As the toner used in the present invention is free from magnetic materials exposed to the surface thereof, the toner exhibits a high chargeability so that it is liable to exhibit a lower developing performance if it contains less than 0.2 wt. % of electroconductive fine powder.

[0271]

Further, in case where the magnetic toner is used in the image forming method including a developing-cleaning step (a step having functions of developing and residual toner-cleaning simultaneously) if the amount is less than 0.2 wt. %, it becomes difficult to supply the electroconductive fine powder to the charging section at the contact position between the contact charging member and the image-bearing member or in a region proximity thereto in an amount sufficient to well charge the image-bearing member by overcoming the charging obstruction caused by the attachment and mixing of the insulating transfer residual toner, thus being liable to cause charging failure.

[0272]

On the other hand, if the amount of the electroconductive fine powder is above 10 wt. %, the amount of electroconductive fine powder recovered in the developing cleaning step becomes excessively large to result in lower chargeability and developing performance in the developing section, so that difficulties, such as image density lowering and toner scattering are liable to occur. It is further preferred that the electroconductive fine powder is contained in a proportion of 0.5 - 5 wt. % of the entire toner.

[0273]

The electroconductive fine powder may preferably

have a resistivity of at most 10^9 ohm.cm. If the electroconductive fine powder has a resistivity exceeding 10^9 ohm.cm, the developing performance of the magnetic toner is liable to be lowered similarly as above. Further, the effect of promoting the uniform chargeability of the image-bearing member becomes small, even if the electroconductive fine powder is present at the contact position between the charging member and the image-bearing member or in the charging region in the vicinity thereof so as to retain an intimate contact via the electroconductive fine powder between the contact charging member and the image-bearing member when used in an image forming method including the developing-cleaning step.

15 [0274]

In order to sufficiently attain the effect of promoting the chargeability of the image-bearing member owing to the electroconductive fine powder, thereby stably accomplishing good uniform chargeability of the image-bearing member, it is preferred that the electroconductive fine powder has a resistivity lower than the resistivity at the surface or at contact part with the image-bearing member of the contact charging member, more preferably a resistivity of 10^6 ohm.cm. or below.

25 [0275]

The electroconductive fine powder contained in the

magnetic toner of the present invention may preferably have a volume-average particle size (D_v) which is smaller than that of the magnetic toner particles and is at least 0.3 μm .

5 [0276]

If the electroconductive fine powder has a excessively small volume-average particle size, the content of the electroconductive fine powder in the magnetic toner has to be set lower in order to obviate
10 the lowering in developing performance, and if the content is excessively low, an effective amount of the electroconductive fine powder cannot be ensured, thus failing to provide an amount of the electroconductive fine powder sufficient to well effect the charging of
15 the image-bearing member by overcoming the charging obstruction caused by the attachment and mixing of the insulating transfer-residual toner particles with the contact charging member in the charging section at the contact position between the charging member and the
20 image-bearing member or in a region proximity thereto, whereby charging failure is liable to be caused. For this reason, it is further preferred that the volume-average particle size of the electroconductive fine powder is 0.8 μm or larger, particularly 1.1 μm or
25 larger.

[0277]

On the other hand, if the electroconductive fine

powder has a volume-average particle size comparable to or larger than that of the magnetic toner particles, the electroconductive fine powder is liable to be separated from the toner particles, and the supply thereof from the developer vessel to the toner-carrying member becomes insufficient to fail in ensuring a sufficient chargeability. Further, the electroconductive fine powder having dropped off the charging member can interrupt or diffuse exposure light for latent image formation to result in lower image quality due to electrostatic latent image detect.

[0278]

Further, if the volume average particle size is larger than the above-mentioned range, the number of electroconductive fine powder particles per unit weight is reduced, so that it becomes difficult to sufficiently attain the effect of promoting the recovery of the transfer residual toner particles. Further, because of the decrease in number of the electroconductive fine powder particles, in view of the decrease and deterioration of the electroconductive fine powder at a vicinity of the charging member, it becomes necessary to increase the content of the electroconductive fine powder in the developer in order to continually supply the electroconductive fine powder to the charging section and stabilizing the uniform chargeability of the image-bearing member ensured by

intimate contact via the electroconductive fine powder between the image-bearing member and the contact charging member. However, if the content of the electroconductive fine powder is excessively increased, the developer as a whole is liable to have a lower chargeability and developing performance, thus causing image density lowering and toner scattering, especially in a high humidity environment. From these viewpoint, it is further preferred that the volume-average particle size of the developer is 5 μm or smaller.

[0279]

It is also preferred that the electroconductive fine powder is transparent, white or only pale-colored, so that it is not noticeable as fog even when transferred onto the transfer material. This is also preferred so as to prevent the obstruction of exposure light in the latent image-step. It is preferred that the electroconductive fine powder shows a transmittance of at least 30 %, with respect to imagewise exposure light used for latent image formation, as measured in the following manner.

[0280]

A sample of electroconductive fine powder is attached onto an adhesive layer of a one-side adhesive plastic film to form a mono-particle densest layer. Light flux for measurement is incident vertically to the powder layer, and light transmitted through to the

backside is condensed to measure the transmitted quantity. A ratio of the transmitted light to a transmitted light quantity through an adhesive plastic film alone is measured as a net transmittance. The
5 light quantity measurement may be performed by using a transmission-type densitometer (e.g., "310T", available from X-Rite K.K.).

[0281]

The electroconductive fine powder of the present
10 invention may for example comprise: carbon fine powder, such as carbon black and graphite powder; and fine powders of metals, such as copper, gold, silver, aluminum and nickel; metal oxides, such as zinc oxide, titanium oxide, tin oxide, aluminum oxide, indium
15 oxide, silicon oxide, magnesium oxide, barium oxide, molybdenum oxide, iron oxide, and tungsten oxide; and metal compounds such as molybdenum sulfide, cadmium sulfide, and potassium titanate; a complex oxide of these while adjusting particle size and distribute as
20 needed. Among the above, it is preferred that the electroconductive fine powder comprises a non-magnetic inorganic oxide, such as zinc oxide, tin oxide or titanium oxide at least at the surface portion thereof.

[0282]

25 Further, it is also possible to use fine particles of electroconductive inorganic oxide comprising a certain principal metal element further doped with 0.1

to 5 wt. % of an element, such as antimony or aluminum, different from the principal metal element, or fine particles coated with an electroconductive material. Examples of such composite electroconductive fine

5 particles may include: titanium oxide fine particles surface-treated with antimony-tin oxide, antimony-doped stannic oxide fine particles and stannic oxide fine particles.

[0283]

10 Herein, "principal metal element of an oxide" means a principal metal element bonded with oxygen, such as titanium in titanium oxide, and tin in tin oxide.

[0284]

15 An oxygen-deficient state of the above-mentioned electroconductive inorganic oxides may also preferably be used.

[0285]

20 Commercially available examples of electroconductive titanium oxide fine powder coated with antimony-tin oxide may include: "EC-300" (Titan Kogyo K.K.); "ET-300", "HJ-1" and "HI-2" (Ishihara Sangyo K.K.) and "W-P" (Mitsubishi Material K.K.).

[0286]

25 Commercially available examples of antimony-doped electroconductive tin oxide fine powder may include: "T-1" (Mitsubishi Material K.K.) and "SN-100P"

(Ishihara Sangyo K.K.). Commercially available examples of stannic oxide fine powder may include: "SH-S" (Nippon Kagaku Sangyo K.K.). In view of the developing performance, it is particularly preferred to
5 use an aluminum-containing metal oxide and/or an oxygen-deficient state metal oxide.

[0287]

The volume-average particle size and particle size distribution of the electroconductive fine powder in
10 the present invention are based on values measured in the following manner. A laser diffraction-type particle size distribution measurement apparatus ("Model LS-230", available from Coulter Electronics Inc.) is equipped with a liquid module, and the
15 measurement is performed in a particle size range of 0.04 - 2000 μ m to obtain a volume-basis particle size distribution. For the measurement, a minor amount of surfactant is added to 10 cc of pure water and 10 mg of a sample electroconductive fine powder is added
20 thereto, followed by 10 min. of dispersion by means of an ultrasonic disperser (ultrasonic homogenizer) to obtain a sample dispersion liquid, which is subjected to a single time of measurement for 90 sec.

[0288]

25 The particle size and particle size distribution of the electroconductive fine powder used in the present invention may for example be adjusted by

setting the production method and conditions so as to
product primary particles of the electroconductive fine
powder having desired particle size and its
distribution. In addition, it is also possible to
5 agglomerate smaller primary particles or pulverize
larger primary particles or effect classification. It
is further possible to obtain such electroconductive
fine powder by attaching or fixing electroconductive
fine particles onto a portion or the whole of base
10 particles having a desired particle size and its
distribution, or by using particles of desired particle
size and distribution containing an electroconductive
component dispersed therein. It is also possible to
provide electroconductive fine powder with a desired
15 particle size and its distribution by combining these
methods.

[0289]

In the case where the electroconductive fine
powder is composed of agglomerate particles, the
20 particle size of the electroconductive fine powder is
determined as the particle size of the agglomerate.
The electroconductive fine powder in the form of
agglomerated secondary particles can be used as well as
that in the form of primary particles. Regardless of
25 its agglomerated form, the electroconductive fine
powder can exhibit its desired function of charging
promotion by presence in the form of the agglomerate in

the charging section at the contact position between the charging member and the image-bearing member or in a region in proximity thereto.

[0290]

5 The resistivity of electroconductive fine powder may be measured by the tablet method and normalized. More specifically, ca. 0.5 g of a powdery sample is placed in a cylinder having a bottom area of 2.26 cm^2 and sandwiched between an upper and a lower electrode
10 under a load of 15 kg. In this state, a voltage of 100 volts is applied between the electrodes to measure a resistance value, from which a resistivity value is calculated by normalization.

[0291]

15 It is another preferred embodiment of the magnetic toner used in the present invention that it further contains close-to-spherical inorganic or organic fine particles having primary particle size exceeding 30 nm (preferably $S_{\text{BET}} < 50 \text{ m}^2/\text{g}$), more preferably of 50 nm or
20 larger ($S_{\text{BET}} < 30 \text{ m}^2/\text{g}$). For example, spherical silica particles, spherical polymethylsilsesquioxane particles or spherical resin particles, may preferably be used.

[0292]

 The toner used in the present invention can
25 further contain other additives within an extent of not adversely affecting the performances thereof. Examples of such additives may include: lubricating powder such

as, powders of polytetrafluoroethylene, zinc stearate and polyvinylidene fluoride; abrasives, such as powders of cerium oxide, silicon carbide and strontium titanate; flowability-improving agents, such as powders
5 of titanium oxide, and aluminum oxide; anti-caking agents; and a small amount of organic or inorganic fine powder of opposite polarity chargeability as a developing performance-improver. These additives can be added after surface hydrophobization.

10 [0293]

The particle size of these additives may be determined by observation through a scanning electron microscope similarly as the above-mentioned inorganic fine powder.

15 [0294]

Next, the image forming system (method and apparatus) of the present invention will be described.

The image forming method according to the present invention, includes: a charging step of charging an
20 image-bearing member by charging means comprising a charging member abutted against the image-bearing member at a contact nip; a latent-image forming step of forming an electrostatic latent image on the charged image-bearing member; a developing step of transferring
25 a magnetic toner carried on a toner-carrying member onto the electrostatic latent image to develop the latent image, thereby forming a magnetic toner image on

the image-bearing member, and a transfer step of electrostatically transferring the magnetic toner image on the image-bearing member onto a transfer material via or without via an intermediate transfer member; 5 wherein the image-bearing member comprises an electroconductive support and a photoconductor layer comprising a silicon-based non-single crystal material and disposed on the electroconductive support, and is charged to a potential of 250 to 600 volts in terms of 10 an absolute value via the charging member.

[0295]

In a preferred embodiment, the developing step is also operated to function as a cleaning step for recovering transfer residual toner remaining on the 15 image-bearing member after transfer of a toner image onto a transfer material (a developing-cleaning step).

[0296]

The image forming method including such a developing-cleaning step will be first described. The 20 image forming method may also be referred to as a cleanerless image forming method.

[0297]

More specifically, the cleanerless image forming method includes: a charging step of charging an image- 25 bearing member by charging means comprising a charging member supplied with a voltage and abutted against the image-bearing member at a contact nip; a latent-image

forming step of forming an electrostatic latent image on the charged image-bearing member; a developing step of transferring a magnetic toner carried on a toner-carrying member onto the electrostatic latent image to
5 develop the latent image, thereby forming a magnetic toner image on the image-bearing member, and a transfer step of electrostatically transferring the magnetic toner image on the image-bearing member onto a transfer material via or without via an intermediate transfer
10 member, which steps are included in a cycle to be repeated for image formation on the transfer material; wherein the developing step is also operated to function as a cleaning step for recovering transfer residual toner remaining after the transfer of the
15 toner image onto the transfer material, and electroconductive fine powder contained in the magnetic toner is attached to the image-bearing member in the developing step and allowed to remain on the image-bearing member after the transfer step to reach a
20 charging section formed at the contact nip between the charging member and the image-bearing member and/or a proximity thereto.

[0298]

Now, the behavior or movement of the magnetic
25 toner particles and the electroconductive fine powder externally added thereto to form the magnetic toner is described.

[0299]

The electroconductive fine powder contained in the magnetic toner is transferred in an appropriate amount thereof together with the magnetic toner particles forming a toner image from the toner-carrying member onto the image-bearing member for development of an electrostatic latent image on the image-bearing member in the developing step.

[0300]

10 The toner image formed on the image bearing member is transferred onto a transfer material (via or without via an intermediate transfer member) in the transfer step. A minor portion of the electroconductive fine powder can also be transferred onto the transfer material side, but the remaining major portion thereof remains attached on the image-bearing member. More specifically, in the case of effecting the transfer of the magnetic toner image by applying a bias voltage of a polarity opposite to the charge of the magnetic toner, the toner image is positively transferred electrostatically, whereas the electroconductive fine powder on the image-bearing member is not positively transferred toward the transfer material because of its electroconductivity, so that the major portion thereof remains attached on the image-bearing member.

[0301]

In the cleanerless image forming method, transfer

residual toner and the above-mentioned electroconductive fine powder remaining on the image-bearing member after the transfer step are brought as they are to the charging section formed at the contact nip between the image bearing member and the contact charging member as a result of the movement of the image-bearing member surface to the attached to the contact charging member. Consequently, the image-bearing member is contact-charged in a state where the electroconductive fine powder is present at the contact nip between the image-bearing member and the contact charging member.

[0302]

Owing to the presence of the electroconductive fine powder, an intimate contact and a low contact resistance between the contact charging member and the image-bearing member can be retained regardless of soiling by mixing of the transfer residual toner at the contact nip, thereby allowing an effective charging of the image-bearing member by the contact charging member.

[0303]

The transfer residual toner attached in mixture to the contact charging member is charged to a polarity identical to that of a charging bias voltage applied from the charging member to the image-bearing member owing to the charging bias voltage, and is then

gradually discharged out of the contact charging member, and moved along with the image-bearing member surface to reach a developing section and be recovered thereat in the developing-cleaning step.

5 [0304]

By repetition of the image forming cycle, the electroconductive fine powder contained in the magnetic toner is transferred onto the image-bearing member surface in the developing section and conveyed along
10 with the movement of the image-bearing member surface via the transfer section to reach the charging section, thus effecting a continual supply of the electroconductive fine powder to the charging section. As a result, even if the electroconductive fine powder
15 is lost to some extent by falling-down, the lowering in charging performance thereby is prevented to stably retain good charging performance.

[0305]

As another problem to be solved, in the case of
20 using a toner containing such electroconductive fine powder in an amount sufficient to ensure a good charging performance by overcoming the charging obstruction due to insulating transfer residual toner attached in mixture to the contact charging member by
25 positive presence of the electroconductive fine powder at the contact nip between the image-bearing member and the contact charging member, there can be encountered

with difficulty in ensuring good image quality due to image density lowering and increased fog as a result of a lower toner content in the developer container immediately before the toner replenishment.

5 [0306]

Also in a conventional image forming apparatus equipped with a cleaning mechanism, in the case of using a toner containing electroconductive fine powder, the above-mentioned difficulties of image density
10 lowering and increased fog have occurred at the time when the image formation is continued until the amount of the toner is reduced in the developer vessel, due to a concentration change in the toner mixture caused by a selective consumption or a selective remaining of the
15 electroconductive fine powder in the developing step. As a countermeasure to this problem, it has been known to securely attach the electroconductive fine powder onto the toner particles, thereby reducing the selective consumption or localization of the
20 electroconductive fine powder to prevent the image density lowering and increased fog.

[0307]

In the case of using a toner contains electroconductive fine powder in a cleanerless image
25 forming method, the localization of electroconductive fine powder adversely affects the image forming performances more seriously. Namely, as mentioned

above, a portion of electroconductive fine powder contained in a toner transferred in an appropriate amount to the image-bearing member together with the toner particles is transferred together with the toner image toward the transfer material but the remaining major portion of the electroconductive fine powder remains attached on the image-bearing member. When the transfer is performed by applying a transfer bias voltage, the toner base particles are actively transferred by being pulled to the transfer material side, but electroconductive fine powders on the image-bearing member are not transferred actively to the transfer material side as they are electroconductive, and some are adhered onto the transfer material side, but the rest is adhered and retained on the image-bearing member.

[0308]

In the cleanerless image forming method, the transfer residual toner and the remaining portion of the electroconductive fine powder after the transfer step are moved as they are to reach the charging section. In this instance, the proportion of the electroconductive fine powder reaching the charging section is clearly larger than that in the original toner due to a difference in transferability between the electroconductive fine powder contained in the charging section, and is then gradually discharged and

5 moved together with the transfer residual toner to the developing(-cleaning) section to be recovered thereat. Due to the recovered toner containing a substantially larger proportion of electroconductive fine powder, the localization or concentration disturbance by the electroconductive fine powder can be remarkably accelerated to result a remarkable lowering in image density affecting the image quality.

[0309]

10 For overcoming the problem of localization or concentration change, if the above-mentioned measure of secure attachment of electroconductive fine powder onto toner particles adopted in the conventional image forming apparatus equipped with a cleaning mechanisms
15 is similarly adopted in a cleanerless image forming system, the electro-conductive fine powder is transferred together with the toner particles toward the transfer material, thus failing to realize sufficient supply to and presence at the charging
20 section of the electroconductive fine powder. As a result, intimate contact between the charging member and the image-bearing member is failed and the chargeability of the image-bearing member is lowered to result in fog and image soiling. The use of a toner
25 containing electroconductive fine powder in a cleanerless image forming system using a contact charging member has involved such serious difficulties.

[0310]

As a result of our study, it has been clarified that the above-mentioned problem of localization or concentration disturbance due to inclusion of electroconductive fine powder in a toner used in a cleanerless image forming system (which per se is desirable from ecological viewpoints, such as freeness from the occurrence of waste toner, and suppression of discharge products, such as ozone, owing to the inclusion of a contact charging member allowing the direct injection charging mechanism) by using a toner having a weight-average particle size (D4) of 3 - 10 μm as well as the above-mentioned specific circularity requirement.

15 [0311]

A toner having a weight-average particle size of below 3 μm exhibits a lower flowability and a higher liability of movement together with the electroconductive fine powder, thus promoting the transfer of the electroconductive fine powder in the transfer step to reduce the supply of the electroconductive fine powder to the charging section. As a result, the charging obstruction due to the transfer residual toner is predominant, thus resulting in fog and image soiling.

[0312]

In the case of using a toner having a weight-

average particle size 10 μm or more, the chargeability of the toner particles is liable to be remarkably decreased when the amount of electroconductive fine powder is increased. As a result, if the amount of the
5 electroconductive fine powder is increased to a level sufficient to maintain an intimate contact between the contact charging member and the image-bearing member at the charging section, the chargeability of the toner particles can be excessively lowered to exhibit a lower
10 developing performance. As a result, even by a slight degree of concentration disturbance due to recovery of the toner containing a substantially larger proportion of electroconductive fine powder in the developing-cleaning step, the difficulty of image density lowering
15 leading to inferior image quality occurs. In order to ensure stable chargeability and developing performance, the toner may preferably have a weight-average particle size of 4 - 8.0 μm .

[0313]

20 In this way, the magnetic toner particle of the present invention is preferable to be used in the development and simultaneous cleaning image forming method or cleanerless image forming method, as well as to be used in an image forming apparatus having the
25 development and simultaneous cleaning means.

[0314]

The toner base particles are particles containing

at least binder resin and coloring agent. The toner particles may preferably have a resistivity of at least 10^{10} ohm.cm, more preferably at least 10^{12} ohm.cm. Unless the toner particles show substantially
5 insulating property, it is difficult to satisfy the developing performance and transferability in combination. Further, charge injection into toner particles is liable to occur under a developing electric field, so that the charge of the toner is
10 disturbed to result in fog.

[0315]

Next, the image forming method of the present invention will be described with reference to the drawings. Figs. 2 and 3 illustrate embodiments having
15 a cleaner and no cleaner, respectively, of the image forming apparatus of the present invention.

Fig. 2 shows the case with a cleaner and Fig. 3 shows a case without a cleaner. Hereinafter the description will be made regarding Fig. 2.

20 [0316]

Referring to Fig. 2, the image forming apparatus includes a photosensitive member (photosensitive drum) 1, and a primary charging roller 306, a developing device 307, a transfer charging roller 302, a cleaner
25 312 and conveyer rollers 308a, 30b, disposed surrounding the photosensitive member 1. The photosensitive member 1 is charged by the charging

roller 306 with the aid of electroconductive fine powder applied on the charging roller 306 from an electroconductive fine powder-application mechanism 314, and exposed to laser light L from a laser light source (not shown) to form an electrostatic image thereon, which is then developed with a monocomponent toner T in the developing device 307 to form a toner image thereon. The toner image is transferred onto a transfer material P by the transfer roller 302 abutted against the photosensitive member 1 via the transfer material P. The transfer material P carrying the toner image is then conveyed via a conveyer guide 311 to a fixing device 313, where the toner image is fixed onto the transfer material P. A minor portion of the toner remaining on the photosensitive member 1 after the transfer is then cleaned by the cleaning means 312. Incidentally, the cleaning means can be omitted in a system as shown in Fig. 3 wherein the developing device 307 also functions as a cleaning means for cleaning such transfer residual toner on the photosensitive member.

[0317]

Fig. 4 is an enlarged schematic view of such a developing device.

[0318]

Referring to Fig. 4, the developing device 307 includes a cylindrical toner-carrying member

(hereinafter referred to as "developing sleeve") 12 comprising a non-magnetic metal, such as aluminum or stainless steel, disposed in proximity to a photosensitive member 1. The photosensitive member 1 and the developing sleeve 12 are disposed with a gap of ca. 200 μ m therebetween by a sleeve/photosensitive member gap-retaining member (not shown). Inside the rotatable developing sleeve 12, a fixed magnet roller 14 is disposed non-movably and concentrically with the developing sleeve 12.

[0319]

The fixed magnet roller 14 is provided with a plurality of magnetic poles, as shown, including S1 for development, N1 for regulating toner coating amount, S2 for take-in and conveyance of toner and N2 for preventing toner blow-out. As a member for regulating the amount of magnetic toner attached to and conveyed with the developing sleeve a magnetic blade 11a is disposed so as to regulate the amount of magnetic toner conveyed to a developing region depending on a gap between the magnetic blade 11a and the developing sleeve 12. At the developing region, a DC/AC-superposed bias voltage is applied between the photosensitive member 1 and the developing sleeve 12, whereby the toner on the developing sleeve 12 is caused to fly onto the electrostatic latent image on the photosensitive member 1 to form a visible image

thereon.

[0320]

Now, a charging step of the image forming method of the present invention will be described.

5 In the charging step, the image-bearing member (photosensitive member) is charged by a charging member supplied with a voltage and contacting the image-bearing member so as to form a contact nip with the image-bearing member.

10 [0321]

 In the image forming method of the present invention, the above-mentioned electroconductive fine powder is preferably present at the contact nip between the charging member and the image-bearing member, e.g.,
15 by application of electroconductive fine powder on the charging roller from the electroconductive fine powder-application mechanism. Accordingly, the charging member may preferably be provided with elasticity, and electroconductivity so as to charge the image-bearing
20 member while being supplied with a voltage. For this purpose, the charging member may preferably comprise an elastic electroconductive roller, a magnetic brush contact charging member comprising a magnetic brush of magnetically constrained magnetic particles and
25 contacting the image-bearing member, or an electroconductive fiber brush contacting the image-bearing member.

[0322]

From the viewpoint of temporarily recovering transfer residual toner on the image-bearing member and carrying the electroconductive fine powder for
5 advantageously effecting direct injection charging, the contact charging member may preferably comprise an elastic electroconductive roller or a rotatable charging brush roller, as a flexible member.

[0323]

10 If the contact charging member has a flexibility, the electroconductive fine powder is provided with an increased opportunity of contracting the image-bearing member at the contact nip with the image-bearing member, thereby exhibiting an improved direct injection
15 charging performance through a high conductivity. As the contact charging member intimately contacts the image-bearing member via the electroconductive fine powder to rub the image-bearing member surface without gap with the electroconductive fine powder present at
20 the contact nip between the contact charging member and the image-bearing member, the charging of the image-bearing member by the contact charging member is predominantly governed by stable and safe direct injection charging mechanism free from discharge
25 phenomenon, whereby a high charging efficiency not achievable by the conventional roller charging scheme can be realized to provide the image-bearing member

with a potential almost identical to the voltage applied to the contact charging member.

[0324]

It is preferred to provide a relative surface speed difference between the contact charging member and the image-bearing member. As a result, the opportunity of the electroconductive fine powder contacting the image-bearing member at the contact position between the contact charging member and the image-bearing member is remarkably increased, thereby further promoting the direct injection charging to the image-bearing member via the electroconductive fine powder.

[0325]

As the electroconductive fine power is present at the contact position between the contact charging member and the image-bearing member, the electroconductive fine powder exhibits a lubricating effect (i.e., friction-reducing effect), so that it becomes possible to provide such a relative surface speed difference between the contact charging member and the image bearing member without causing a remarkable increase in torque acting between these members or a remarkable abrasion of these members.

[0326]

Such a relative surface speed difference may be provided by rotating the contact charging member and

the image-bearing member with a certain peripheral speed ratio.

[0327]

It is preferred that the charging member and the
5 image-bearing member are moved in mutually opposite
directions at the contact part. This is preferred in
order to enhance the effect of temporarily damming and
leveling the transfer-residual toner particles on the
image-bearing member brought to the contact charging
10 member. This is for example accomplished by driving
the contact charging member in rotation in a direction
and also driving the image-bearing member in rotation
so as to move the surfaces of these members in mutually
opposite directions. As a result, the transfer-
15 residual toner particles on the image-bearing member
are once released from the image-bearing member to
advantageously effect the direct injection charging and
suppress the obstruction of the latent image formation.

[0328]

20 Namely, it is possible to provide a relative
surface speed difference by moving the charging member
and the image-bearing member in the same direction.
However, as the charging performance in the direct
injection charging depends on a moving speed ratio
25 between the image-bearing member and the contact
charging member, a large moving speed is required in
the same direction movement in order to obtain an

identical relative movement speed difference than in the opposite direction movement. This is disadvantageous. Further, the opposite direction movement is more advantageous also in order to attain the effect of leveling the transfer-residual toner particle pattern on the image-bearing member.

[0329]

Such a relative speed difference may be represented by a relative (movement) speed ratio as determined by the following formula:

[Mathematical Formula 4]

Relative speed ratio (%)

$$= |[V_c - V_p] / V_p| \times 100|,$$

wherein V_p denotes a surface moving speed of the image-bearing member, V_c denotes a surface moving speed of the charging member of which the sign is taken positive when the charging member surface moves in the same direction as the image-bearing member surface at the contact position.

The relative (movement) speed ratio is generally in the range of 10 - 500 %.

[0330]

The contact charging member may assume a form of, e.g., a charging roller, a charging blade or an electroconductive brush, and achieves advantages, such as not necessity of using a high voltage and reduction of discharge products, such as ozone.

[0331]

The charging roller or charging blade as a contact charging member may preferably comprise an electroconductive rubber, which may be surface-coated with a release film comprising, e.g., nylon resin, PVdF (polyvinylidene fluoride), PVdC (polyvinylidene chloride) or fluorine-containing acrylic resin, so as to alleviate the attachment of transfer-residual toner.

[0332]

Too low a hardness of the elastic conductive roller results in a lower contact with the image-bearing member because of an unstable shape and abrasion or damage of the surface layer due to the electroconductive fine powder present at the contact part between the charging member and the image-bearing member, thus being difficult to provide a stable chargeability of the image-bearing member. On the other hand, too high a hardness makes it difficult to ensure a contact part with the image-bearing member and results in a poor microscopic contact with the image-bearing member surface, thus making it difficult to attain a stable chargeability of the image-bearing member. From these viewpoints, it is further preferred that the elastic conductive roller has an Asker C hardness of at most 50 deg., more preferably 25 - 50 deg.

[0333]

In addition to the elasticity for attaining a sufficient contact with the image-bearing member, it is important for the elastic conductive roller to function as an electrode having a sufficiently low resistance for charging the moving image-bearing member. On the other hand, in case where the image-bearing member has a surface defect, such as a pinhole, it is necessary to prevent the leakage of voltage. In the case of an image bearing member such as an electrophotographic photosensitive member, in order to have sufficient charging performance and leakage resistance, the elastic conductive roller may preferably have a resistivity of $10^3 - 10^8$ ohm.cm, more preferably $10^4 - 10^7$ ohm.cm.

[0334]

The resistivity values of a roller are based on values measured by pressing the roller against a 30 mm-diameter cylindrical aluminum drum under the total abutting pressure of 1 kg to the roller core metal and applying 100 volts between the core metal of the roller and the aluminum drum.

[0335]

Such an elastic conductive roller may be prepared by forming a medium resistivity layer of rubber or foam material on a core metal. The medium resistivity layer may be formed in a roller shape on the core metal from an appropriate composition comprising a resin (of,

e.g., urethane), conductor particles (of, e.g., carbon black), a vulcanizer and a foaming agent. Thereafter, a post-treatment, such as cutting or surface polishing, for shape adjustment may be performed to provide an
5 elastic conductive roller. The elastic conductive roller may preferably have a surface provided with minute cells or unevennesses so as to stably retain the electroconductive fine powder.

[0336]

10 The cells may preferably have concavities providing an average cell diameter corresponding to spheres of 5 - 300 μm and also a void percentage of the surface of 15 - 90 %.

[0337]

15 If the average cell diameter is below the above mentioned range, the supply of the electroconductive fine powder is liable to be short, and in excess of the above-mentioned range, the durability of the roller member is liable to be impaired. The average cell
20 diameter is a spherical diameter when each cell or surface cavity is regarded as a part of a sphere, and can be measured by a scanning electron microscope. An image analyzer can be used as desired at that time.

[0338]

25 Further, if the void percentage is below the above-mentioned range, the electro-conductive fine powder supply is liable to be short, and in excess of

the above-mentioned range, the durability of the roller member is liable to be short.

[0339]

The elastic conductive roller may be formed of
5 other materials. A conductive elastic material may be provided by dispersing a conductive substance, such as carbon black or a metal oxide, for resistivity adjustment in an elastomer, such as ethylene-propylene-
diene rubber (EPDM), urethane rubber, butadiene-
10 acrylonitrile rubber (NBR), silicone rubber or isoprene rubber. It is also possible to use a foam product of such an elastic conductive material. It is also possible to effect a resistivity adjustment by using an ionically conductive material alone or together with a
15 conductor substance as described above.

[0340]

The elastic conductive roller is disposed under a prescribed pressure against the image-bearing member while resisting the elasticity thereof to provide a
20 charging contact part (or portion) between the elastic conductive roller and the image-bearing member. The width of the contact part is not particularly restricted but may preferably be at least 1 mm, more preferably at least 2 mm, so as to stably provide an
25 intimate contact between the elastic conductive roller and the image-bearing member.

[0341]

The charging member used in the charging step of the present invention may also be in the form of a brush comprising conductive fiber so as to be supplied with a voltage to charge the image-bearing member. The
5 charging brush may comprise ordinary fibrous material containing a conductor dispersed therein for resistivity adjustment. For example, it is possible to use fiber of nylon, acrylic resin, rayon, polycarbonate or polyester.

10 [0342]

Examples of the conductor may include fine powder of electroconductive metals, such as nickel, iron, aluminum, gold and silver; electroconductive metal oxides, such as iron oxide, zinc oxide, tin oxide,
15 antimony oxide and titanium oxide; and carbon black. Such conductors can have been surface-treated for hydrophobization or resistivity adjustment, as desired. These conductors may appropriately be selected in view of dispersibility with the fiber material and
20 productivity.

[0343]

The charging brush as a contact charging member may include a fixed-type one and a rotatable roll-form one. A roll-form charging brush may be formed by
25 winding a tape to which conductive fiber pile is planted about a core metal in a spiral form. The conductive fiber may have a thickness of 1 - 20 denier

(fiber diameter of ca. 10 - 500 μm) and a brush fiber length of 1 - 15 mm arranged in a density of 10^4 - 3×10^5 fibers per inch (1.5×10^7 - 4.5×10^8 fibers per m^2).
[0344]

5 The charging brush may preferably have as high a density as possible. It is also preferred to use a thread or fiber composed of several to several hundred fine filaments, e.g., threads of 300 denier/50 filaments, etc., each thread composed of a bundle of 50
10 filaments of 300 denier. In the present invention, however, the charging points in the direct injection charging are principally determined by the density of electroconductive fine powder present at the contact part and in its vicinity between the charging member
15 and the image-bearing, so that the latitude of selection of charging member materials has been broadened.
[0345]

20 Similarly as the elastic conductive roller, the charging brush may preferably have a resistivity of 10^3 - 10^8 ohm.cm, more preferably 10^4 - 10^7 ohm.cm so as to provide sufficient chargeability and leakage resistance of the image-bearing member.
[0346]

25 Commercially available examples of the charging brush materials may include: electroconductive rayon fiber "REC-B", "REC-C", "REC-M1" and "REC-M10"

(available from Unitika K.K.), "SA-7" (Toray K.K.),
"THUNDERRON" (Nippon Sanmo K.K.), "BELTRON" (Kanebo
K.K.), "KURCARBO" (carbon dispersed rayon, Kuraray
K.K.) and "ROABAL" (Mitsubishi Rayon K.K.), "REC-B",
5 "REC-C", "REC-M1" and "REC-M10" are particularly
preferred in view of environmental stability.

[0347]

Next, the amount of electroconductive fine powder
present at the contact position between the image-
10 bearing member and the contact charging member will be
described.

[0348]

If the amount of electroconductive fine powder
present at the contact position between the image-
15 bearing member and the contact charging member is too
small, the lubricating effect of the electroconductive
fine powder cannot be sufficiently attained but results
in a large friction between the image-bearing member
and the contact charging member, so that it becomes
20 difficult to drive the contact charging member in
rotation with a speed difference relative to the image-
bearing member. As a result, the driver torque
increases, and if the contact charging member is
forcibly driven, the surfaces of the contact charging
25 member and the image-bearing member are liable to be
abraded. Further, as the effect of increasing the
contact opportunity owing to the electroconductive fine

powder is not attained, it becomes difficult to attain a sufficient chargeability of the image bearing member. On the other hand, if the electroconductive fine powder is present in an excessively large amount, the falling
5 of the electroconductive fine powder from the contact charging member is increased, thus being liable to cause adverse effects, such as obstruction of latent image formation as by interception of imagewise exposure light.

10 [0349]

In view of the above, the amount of the electroconductive fine powder at the contact position between the image-bearing member and the contact charging member is preferably at least 10^3
15 particles/mm², more preferably $10^3 - 5 \times 10^5$ particles/mm², further preferably $10^4 - 5 \times 10^5$ particles/mm². Below 10^3 particles/mm², it becomes difficult to attain sufficient lubrication effect and opportunity of contact, thus being liable to result in
20 a lower chargeability. Below 10^4 particles/mm², some lowering in chargeability can occur in case of an increased amount of transfer residual toner.

[0350]

The appropriate range of amount of the
25 electroconductive fine powder on the image-bearing member in the charging step, is also determined depending on a density of the electroconductive fine

powder affecting the uniform charging on the image-bearing member. It is needless to say that the image-bearing member has to be charged more uniformly than at least a recording resolution. However, in view of a human eye's visual characteristic, at spatial frequencies exceeding 10 cycles/mm, the number of discriminatable gradation levels approaches infinitely to 1, that is, the discrimination of density irregularity becomes impossible. As a positive utilization of this characteristic, in the case of attachment of the electroconductive fine powder on the image-bearing member, it is effective to dispose the electroconductive fine powder at a density of at least 10 cycles/mm and effect the direct injection charging.

[0351]

Even if charging failure is caused at sites with no electroconductive fine powder, an image density irregularity caused thereby occurs at a spatial frequency exceeding the human visual sensitivity, so that no practical problem is encountered on the resultant images.

[0352]

As to whether a charging failure is recognized as density irregularity in the resultant images, when the application density of the electroconductive fine powder is changed, only a small amount (e.g., 10 particles/mm²) of electroconductive fine powder can

exhibit a recognized effect of suppressing density irregularity, but this is insufficient from a viewpoint as to whether the density irregularity is tolerable to human eyes.

5 [0353]

However, an application amount of 10^2 particles/mm² results in a remarkably preferable effect by objective evaluation of the image. Further, an application density of 10^3 particles/mm² or higher
10 results in no image problem at all attributable to the charging failure. In the charging step based on the direct injection charging mechanism as basically different from the one based on the discharge charging mechanism, the charging is effected through a positive
15 contact between the contact charging member and the image-bearing member, but even if the electroconductive fine powder is applied in an excessively large density, there always remain sites of no contact. This however, results in practically no problem by applying the
20 electroconductive fine powder while positively utilizing the above-mentioned visual characteristic of human eyes.

[0354]

However, the application of the direct injection
25 charging scheme for uniform charging of the image-bearing member in a developing-cleaning image forming method causes a lowering in charging performance due to

attachment and mixing with the charging member of the transfer residual toner. For suppressing the attachment and mixing with the charging member of transfer residual toner and overcoming the charging obstruction thereby to well effect the direct injection charging, it is preferred that the electroconductive fine powder is present at a density of 10^4 particles/mm² or higher at the contact position between the image-bearing member and the contact charging member.

[0355]

The upper limit of the amount of the electroconductive fine powder present on the image-bearing member is determined by the formation of a densest mono-particle layer of the electroconductive fine powder. In excess of the amount, the effect of the electroconductive fine powder is not increased, but an excessive amount of the electroconductive fine powder is liable to be present on the image-bearing member after the charging step, thus causing difficulties, such as interruption or scattering of imagewise exposure light.

[0356]

Thus, a preferable upper amount of the electroconductive fine powder may be determined as an amount giving a densest mono-particle layer of the electroconductive fine powder on the image-bearing

member while it may depend on the particle size of the electroconductive fine powder and the retentivity of the electroconductive fine powder by the contact charging member.

5 [0357]

More specifically, if the electroconductive fine powder is present on the image-bearing member at a density in excess of 5×10^5 particles/mm² while it depends on the particle size of the electroconductive fine powder, the amount of the electroconductive fine powder falling off the image-bearing member is increased to soil the interior of the image forming apparatus, and the exposure light quantity is liable to be insufficient regardless of the light-transmissivity of the electroconductive fine powder. If the amount is suppressed to be 5×10^5 particles/mm² or below, the amount of falling particles soiling the apparatus is suppressed and the exposure light obstruction can be alleviated. As an experimental result, the amount of the electroconductive fine powder in the above-mentioned range at the contact part between the image bearing member and the contact charging member resulted in amounts of electroconductive fine powder falling on the image-bearing member (i.e., the amount of electroconductive fine powder on the image-bearing member in the latent image forming step)(in the range of $10^2 - 10^5$ particles/mm². Also in view of adverse

effect for latent image formation, a preferred range of the electroconductive fine powder at the contact part between the charging member and the image-bearing member is $10^4 - 5 \times 10^5 / \text{mm}^2$.

5 [0358]

The amounts of the electroconductive fine powder at the charging contact part and on the image bearing member in the latent image forming step described herein are based on values measured in the following
10 manner. Regarding the amount of the electroconductive fine powder at the contact part, it is desirable to directly measure the value at the contacting surfaces on the contact charging member and the image-bearing member. However, in the case of opposite surface
15 moving directions of the contact charging member and the image-bearing member, most particles present on the image-bearing member prior to the contact with the contact charging member are peeled off by the charging member contacting the image-bearing member while moving
20 in the reverse direction, so that the amount of the electroconductive fine powder present on the contact charging member just before reaching the contact part is taken herein as the amount of electroconductive fine powder at the contact part.

25 [0359]

More specifically, in the state of no charging bias voltage application, the rotation of the image-

bearing member and the elastic conductive roller is stopped, and the surfaces of the image-bearing member and the elastic conductive roller are photographed by a video microscope ("OVM 1000N", made by Olympus K.K.)
5 and a digital still recorder ("SR-310", made by Deltis K.K.).

[0360]

For the photographing, the elastic conductive roller is abutted against a slide glass under an
10 identical condition as against the image-bearing member, and the contact surface is photographed at 10 parts or more through the slide glass and an objective lens having a magnification of 1000 of the video microscope. The digital images thus obtained are
15 processed into binary data with a certain threshold for regional separation of individual particles, and the number of regions retaining particle fractions are counted by an appropriate image processing software. Also the electroconductive fine powder on the image-
20 bearing member is similarly photographed through the video microscope and the amount thereof is counted through similar processing.

[0361]

In the charging step of the image forming method
25 of the present invention, an electroconductive contact charging member (or contact charger) such as a charging roller or a fur brush charger, a magnetic brush charger

or a blade charger (charging blade), is caused to contact a photosensitive member (a member-to-be-charged, an image-bearing member) and is supplied with a prescribed charging bias voltage to charge the
5 photosensitive member surface to a prescribed potential of a prescribe polarity. The charging bias voltage applied to the contact charging member may be a DC voltage alone for exhibiting a good charging performance or also a superposition of a DC voltage and
10 an AC voltage (alternating voltage).

[0362]

The AC voltage may have an appropriate voltage, waveform such as a sine wave, a rectangular wave, a triangular wave, etc. Further, the AC voltage may
15 comprise a pulse wave formed by periodically turning on and off a DC voltage supply. Thus, for the AC voltage, a bias that may have periodically changing voltages can be used.

[0363]

20 In the present invention, it is preferable that the charging member is abutted to the photosensitive member, and this is a preferable embodiment in terms of environmental protection as no ozone is generated.

[0364]

25 The AC voltage may preferably have a peak voltage of below $2 \times V_{th}$ (V_{th} : discharge initiation voltage at the time of DC voltage application). If this condition

is not satisfied, the potential on the image-bearing member is liable to be unstable.

[0365]

5 The AC voltage applied in superposition with a DC voltage may more preferably have a peak voltage below V_{th} so as to charge the image-bearing member without being substantially accompanied with a discharge phenomenon.

[0366]

10 As preferred conditions for driving a charging roller, the roller may be abutted at a pressure of 4.9 - 490 N/m (5 - 500 g/cm) and supplied with a DC voltage alone or in superposition with an AC voltage. The DC/AC-superposed voltage, for example, may preferably
15 comprise an AC voltage of 0.5 - 5 kV (V_{pp}) and a frequency of 50 Hz to 5 kHz, and a DC voltage of ± 0.2 - ± 5 kV.

[0367]

20 Next, the charging step in which magnetic particles present in the contact point formed by the charging member with the image-bearing member will be described.

In another preferred embodiment of the present invention, the charging step may be operated by using a
25 magnetic brush charger comprising a brush of magnetically constraint magnetic particles abutted against the image-bearing member surface and supplied

with a voltage to charge the image-bearing member surface.

[0368]

More specifically, such a magnetic brush charger
5 may comprise a magnet roller as a magnetic force-
generating means, a non-magnetic electroconductive
sleeve of, e.g., aluminum, stainless steel or an
electroconductive resin, disposed rotatably so as to
cover an outer periphery of the magnet roller, and a
10 layer of magnetic particles (magnetic brush) held in
attachment onto the electroconductive sleeve under a
magnetic force exerted by the magnet roller. The
magnetic brush is caused to contact the image-bearing
member and charge the image-bearing member surface by
15 applying a voltage to the electroconductive sleeve.

[0369]

Hereinafter, magnetic particles constructing a
magnetic brush will be described.

The magnetic brush is composed of magnetic
20 particles which comprise electroconductive and
magnetically susceptible materials, such as single or
mixture crystals like ferrite and magnetite. It is
also possible to use conductive and magnetic particles
formed of a kneaded mixture of electroconductive and
25 magnetic fine powder with a binder polymer, optionally
further coated with a resin layer. Among the above,
ferrite particles are preferred, and the ferrite may

suitably comprise a metal element, such as copper, zinc, manganese, magnesium, iron, lithium, strontium or barium.

[0370]

5 The magnetic particles may preferably have a saturation magnetization of 15 to 70 Am²/kg. If the saturation magnetization exceeds 70 Am²/kg, because of an excessively large magnetic constraint force, the resultant magnetic brush becomes hard to be prevented
10 from free movement, thus being liable to cause a lower conductivity and charging failure and also promote the wearing of the photosensitive member. If the saturation magnetization is below 15 Am²/kg, the magnetic constraint force is lowered, and the magnetic
15 particles transferred onto the photosensitive member is liable to remain on the photosensitive member without being returned to the magnetic brush, thus causing difficulties, such as charging failure due to reduction of the magnetic particles, and adverse effects on the
20 developing, transfer and fixing steps.

[0371]

 The saturation magnetization values described herein are based on values measured under a magnetic field of 1 kilo-oersted by using an oscillating
25 magnetometer 8"VSM-35-15", made by Toei Kogyo K.K.).

[0372]

 The average particle size of the magnetic

particles may preferably have 10 - 50 μm in an average particle size. Below 10 μm , the magnetic particles in the brush are liable to attach to the photosensitive member, and the conveyability of the magnetic particles forming the brush is liable to be impaired. Above 50 μm , the contact points between the magnetic particles and the photosensitive member are reduced, thus being liable to lower the uniformity of the injection charging performance. An average particle size of 15 - 30 μm is further preferred.

[0373]

Such an average particle size may be adjusted by control of production conditions or by an adjustment of particle size distribution as by classification after the production.

[0374]

The classification method and apparatus used for production of magnetic particles are not particularly limited. In order to obtain a desired particle size efficiently, it is preferred use a sloped inertia classifier such as "Elbow Jet", a centrifugal separator, such as "Dispersion Separator" or "Turboplex", or sieving.

[0375]

The volume-basis average particle size and particle size distribution of magnetic particles described herein are based on values measured by using

a laser diffraction-type particle size distribution meter ("HELOS", made by Nippon Denshi K.K.) combined with a dry dispersion unit ("RODOS", made by Nippon Denshi K.K.) under the conditions of a lens focal distance of 200 mm, dispersion pressure of 300 kPa and a measurement time of 1-2 sec to effect a measurement in a range of 0.5 μ m to 350.0 μ m divided into 31 channels to measure the number of particles in each channel and determining a particle size giving a 50 %- volume on an accumulative volume-particle size curve as a median particle size (Dv.50%) and % by volume values of particles for respective particle size ranges.

[0376]

The laser diffraction-type particle size distribution meter ("HELOS") is an apparatus for measurement based on the Franhofer's diffraction principle wherein sample particles are illuminated with laser light from a laser light source to form a diffraction image on a lens focal plane on the opposite side from the light source, and the diffraction image is detected and processed to determine a particle size distribution of the sample particles.

[0377]

The magnetic particles may preferably have a volume resistivity of 10^4 to 10^9 ohm.cm. Below 10^4 ohm.cm, the pinhole leakage is liable to occur, and above 10^9 ohm.cm, the photosensitive member is liable

to be charged insufficiently. In view of the leakage through magnetic particles, it is further preferred that the charger magnetic particles have a resistivity of 10^6 ohm.cm. or higher.

5 [0378]

The volume resistivity values of magnetic particles described herein are based on values measured by placing an amount of magnetic particles between upper and lower electrodes of 2 cm^2 in area so as to
10 form a thickness of 1 mm under a load of 1 kg on the upper electrode and applying an voltage of 100 volts between the electrodes in an environment of 23 °C/65 %RH. From a measured current value, the resistivity is calculated.

15 It is further preferred that the magnetic particles exhibit little resistivity difference between smaller and larger particle sizes.

[0379]

The magnetic particles may preferably be coated
20 with a surface layer for controlling the resistivity and triboelectric chargeability. The surface layer may assume, e.g., a vapor deposition film, a resin film, an electroconductive resin film, a resin film with an electroconductive agent dispersed therein, or a
25 coupling agent film.

[0380]

The surface layer need not completely coat the

magnetic particles, but the magnetic particles can be partially exposed, e.g., can be coated with a discrete film.

[0381]

5 The resin forming the surface coating layer may for example comprise: homopolymers or copolymers of monomers, inclusive of styrene monomers, such as styrene and chlorostyrene; olefins, such as ethylene, propylene, butylenes and isobutylene; vinyl esters,
10 such as vinyl acetate, vinyl propionate, vinyl benzoate, and vinyl butyrate; α -methylene aliphatic monocarboxylate, such as methyl acrylate, ethyl acrylate, butyl acrylate, dodecyl acrylate, octyl acrylate, phenyl acrylate, methyl methacrylate, ethyl
15 methacrylate, butyl methacrylate, and dodecyl methacrylate; vinyl esters, such as vinyl methyl ether, vinyl ethyl ether and vinyl butyl ether; and vinyl ketones, such as vinyl methyl ketone, vinyl hexyl ketone, and vinyl isopropenyl ketone. Particularly, in
20 view of the dispersion of electroconductive fine particles and film formability and productivity of the coating layer, polystyrene, styrene-alkyl acrylate copolymers, styrene-acrylonitrile copolymer, styrene-butadiene copolymer, styrene-maleic anhydride
25 copolymer, polyethylene and polypropylene are preferred. It is also preferred to use polycarbonate resin, phenolic resin, polyester, polyurethane, epoxy

resin, polyolefin, fluorine-containing resin, silicone resin or polyamide.

[0382]

Examples of the fluorine-containing resin may
5 include: polyvinyl fluoride, polyvinylidene fluoride, polytrifluoroethylene, polychlorotrifluoroethylene, polydichlorodifluoroethylene, polytetrafluoroethylene and polyhexafluoropropylene, and solvent-soluble copolymers of these monomers with another monomer.

10 Examples of electroconductive agent dispersed in the surface layer-forming resin may include: ionically conductive powders inclusive of powders of metals, such as copper, nickel, iron, aluminum gold and silver; metal oxides, such as iron oxide, ferrite, zinc oxide,
15 tin oxide, antimony oxide, and titanium oxide; and carbon black; and further ionic conductive agents, such as lithium perchlorate, and tetraammonium salts.

[0383]

Examples of the coupling agent may include:
20 titanate coupling agents, such as isopropoxytriisostearoyl titanate, dihydroxybis(lactate)titanium, and diisopropoxybis(acetylacetonato)titanium; aluminum coupling agents, such as acetoalkoxyaluminum diisopropylate; and silane coupling agents, such as
25 dimethylaminopropyltrimethoxysilane, n-octadecyldimethylmethoxysilane, n-hexyltriethoxysilane, 3-aminopropyltrimethoxysilane and n-octadecyltri-

methoxysilane. It is possible to introduce a functional group, such as amino or fluoro. The coating with a layer of coupling agent allows the formation of a very thin film of molecular order on the surface of magnetic particles, thus little affecting the resistivity of the magnetic particles, so that the resistivity control of the coating layer need not be effected if the resistivity of the core magnetic particles has been adjusted.

10 [0384]

A characteristic feature of the image forming system of the present invention resides in the use of a photosensitive member comprising an electroconductive support and an Si-based non-single crystal photoconductor layer (hereinafter representatively called an "a-Si (photosensitive) layer" formed on the electroconductive support. The photosensitive member may be representatively called an "a-Si photosensitive member" sometimes.

20 [0385]

The a-Si photosensitive member used in the present invention comprises an electroconductive support and a photosensitive layer of Si-based non-single crystal material (which may be typically amorphous but can be microcrystalline or poly-crystalline to some extent unlike a single crystal material) formed on the electroconductive support, and those with enhanced

characteristics are used as needed.

[0386]

It is possible to dispose a lower charge injection-barrier layer below the a-Si photosensitive layer, so as to prevent the charge injection from the support. It is also possible to dispose an upper charge injection barrier layer, an interference-prevention layer (or reflection-prevention layer) or a surface layer, above or below the photosensitive layer, as desired.

[0387]

In order to have desired properties, the a-Si layer may be formed by incorporating one or more of other doping elements, inclusive of: hydrogen; group III elements, such as boron, aluminum and gallium; group IV elements, such as germanium and tin; group V elements, such as nitrogen, phosphorus and arsenic; group VII elements, such as oxygen, sulfur and selenium; halogen atoms, such as fluorine, chlorine and bromine. An a-Si photosensitive member functioning as a negatively charged image-bearing member may be formed as a combination of layers having controlled properties; e.g., as a combination of a hydrogen-containing a-Si layer as a photosensitive layer, a phosphorus-doped hydrogen-containing a-Si layer as a lower charge injection barrier layer and a boron-doped hydrogen-containing a-Si layer as an upper charge

injection-barrier layer.

[0388]

Hereinbelow, some specific examples of image-bearing member in the present invention will be
5 described with reference to Figs. 5 and 6.

[0389]

Figs. 5 and 6 is an example of schematic cross-sectional views of the image-bearing member to be used in the present invention. Fig. 5 shows a single layer-
10 type photosensitive member including a single photoconductor layer, and Fig. 6 shows a function separation-type photosensitive member including a photoconductor layer functionally separated into a charge generation layer and a charge transport layer.

15 [0390]

More specifically, the a-Si photosensitive member shown in Fig. 5 includes an electroconductive support 201 of, e.g., aluminum, and a charge injection barrier layer 202, a photoconductor layer 203 and a surface
20 layer 204 successively formed on the electroconductive support 201. The charge injection barrier layer 202 may be disposed as desired for preventing charge injection from the electroconductive support 201 to the photoconductor layer 203. The photoconductor layer 203
25 comprises at least Si-based non-single crystal material and exhibits photoconductivity. The surface layer 204 may be disposed as desired for retaining a developed

image thereon.

[0391]

The following description will be made on an assumption that the charge injection barrier layer 202 and the surface layer 204 are present except for a case where the presence or absence of the charge injection barrier layer and the surface layer 204 affects the performances concerned.

The a-Si photosensitive member shown in Fig. 6 includes a laminate photoconductor layer 203 which is functionally separated into a charge transport layer 206 comprising an amorphous material containing at least silicon and carbon atoms and a charge generation layer 205 comprising an amorphous material containing at least silicon atom. When the photosensitive member is exposed to light, carriers principally generated in the charge generation layer 205 are passed through the charge transport layer 206 to reach the electroconductive support 201.

[0392]

The surface layer 204 may be formed from gas, such as CH_4 , C_2H_6 , C_3H_8 or C_4H_{10} or a gassifiable hydrocarbon. Such a carbon-source gas may be diluted with a gas, such as H_2 , He, Ar and Ne.

[0393]

The electroconductive support 201 may comprise an electro-conductive or -nonconductive substrate. The

electroconductive support may be composed of an electroconductive substrate comprising: a metal, such as Al, Cr, Mo, Au, In, Nb, Ge, V, Ti, Pt, Pd or Fe, or an alloy of these metals, such as stainless steel.

- 5 Alternatively, the electroconductive support may also be formed by coating at least a side of forming a photosensitive layer of an insulating substrate, such as a film or sheet of synthetic resins, such as polyester, polyethylene, polycarbonate, cellulose
10 acetate, polypropylene, polyvinyl chloride, polystyrene or polyamide, or glass or ceramic sheet, with an electroconductive layer.

[0394]

- The electroconductive support 201 may assume a
15 form of a cylinder or an endless belt having a smooth or uneven surface. The thickness thereof may be appropriately determined so as to provide a desirable image-bearing member but may ordinarily be at least 10 μm in view of the production, processing and mechanical
20 strength of the electroconductive support 201.

[0395]

- Particularly, in the case of using coherent light such as laser light capable of causing interferential fringes appearing as image defects in developed images,
25 the electroconductive support 201 may be provided with surface unevennesses within an extent of not causing substantial reduction of photogenerated carriers in a

manner as described in JP-A 60-168156, JP-A 60-178457, JP-A 60-225854 and JP-A 61-231561.

[0396]

As another method of obviating image defect such
5 as interferential fringes caused by coherent light such as laser light, it is possible to dispose an interference-prevention layer, such as a light absorbing layer, or a like region, within or below the photosensitive layer.

10 [0397]

Further, by imparting minute scars onto the electroconductive support surface, the surface roughness of the photosensitive member surface can be controlled. Such scars may be provided by using an
15 abrasive, chemical etching, so-called dry etching in plasma, or sputtering. The depth and size of the scars thus formed may be controlled so as not to cause a substantial decrease in photogenerated carriers.

[0398]

20 The photoconductor layer 203 as a part of photosensitive layer may be formed by a vacuum film deposition process under controlled conditions for providing a desired property on the electroconductive support 201 or optionally on the charge injection
25 barrier layer 202.

[0399]

More specifically, various vacuum film deposition

processes, inclusive of glow discharge processes (AC-discharge CVD, such as low frequency CVD, high-frequency CVD, and microwave CVD, or DC-discharge CVD), sputtering, vacuum evaporation, ion plating, photo-CVD, and thermo-CVD, may be used. These vacuum film deposition processes and conditions thereof may be appropriately selected, in view of investment costs, production scale and desired properties of the resultant photosensitive members, but it is generally suitable to use a glow discharge process, particularly a high-frequency glow discharge process using power source frequency of RF-band, μ W-band or VHF-band.

[0400]

As is well known, the formation of a photoconductor layer 203 by the glow discharge process may basically be performed by introducing an Si-supply source gas for supplying silicon (Si) atoms, an H-supply source gas for supplying hydrogen (H) atoms and/or an X-supply source gas for supplying halogen (X) atoms into a reaction vessel placeable in a reduced pressure to cause glow discharge therein, thereby forming layer of a-Si; H, X on an electroconductive support 201 disposed in advance at a prescribed position in the vessel.

[0401]

In order to compensate for dangling bonds of silicon atoms to provide the layer with improved

performances, particularly photoconductivity and charge retention characteristic, it is necessary to have the photoconductive layer 203 contain hydrogen atoms or/and halogen atoms in a proportion of preferably 10 - 30
5 atomic %, more preferably 15 - 25 atomic %, with respect to the total amount of silicon, and hydrogen or/and halogen.

[0402]

In order to structurally incorporate hydrogen into
10 the photoconductor layer at a controlled percentage so as to form a layer of desired properties, it is desirable to further introduce gas stream of H₂ and or He or a hydrogen-containing silicon compound in a desired mixing ratio. Each source gas can comprise a
15 single species or a mixture of several species in a desired ratio.

[0403]

Preferred halogen-supply source gas used in the present invention may include: gaseous or gassifiable
20 halogen compounds, such as halogen gas, halogen compounds, and halogen-substituted silane derivatives. It is also possible to use a gaseous or gassifiable halogen containing hydrogenated silicon compound containing both silicon and halogen. Suitable examples
25 of the halogen compounds usable in the present invention may include: fluorine gas (F₂), and inter-halogen compounds, such as BrF, ClF, ClF₃, BrF₃, BrF₅,

IF₃ and IF₇.

[0404]

Suitable examples of the halogen-containing silicon compounds or so-called halogen-substituted
5 silane derivative may include: silicon fluorides, such as SiF₄ and Si₂F₆.

[0405]

The content(s) of hydrogen atom or/and halogen atom contained in the photoconductor layer may be
10 adjusted by controlling the temperature of the electroconductive support 201, rates of introduction of hydrogen- or/and halogen-source gas into the reaction vessel and the intensity of discharge power supply.

[0406]

15 The photoconductor 203 may preferably contain a conductivity-controlling atom, which can be contained uniformly in the photoconductor layer 203 or in different concentration in a thickness direction.

[0407]

20 The conductivity-controlling atom may be a so-called impurity as used in the semiconductor field, and may be a group IIIb atom in the periodic table for providing a p-type conductivity or a group Vb atom on the periodic table for providing an n-type
25 conductivity.

[0408]

The group IIIb atoms may include: boron (B),

aluminum (Al), gallium (Ga), indium (In) and tallium (Tl), and particularly suitably be B, Al and Ga. The group Vb atoms may include: phosphorus (P), arsenic (As), antimony (Sb) and bismuth, and particularly suitably be P and As.

[0409]

The conductivity-controlling atom may preferably be contained in the photoconductor layer 203 at a concentration of 1×10^{-2} - 1×10^4 atom.ppm, more preferably 5×10^{-2} - 5×10^3 atom.ppm, particularly 1×10^{-1} - 1×10^3 atom.ppm.

[0410]

For introducing the group IIIb atom or group Vb atom into the photoconductor layer 203, a IIIb atom-source compound or a Vb atom-source compound may be introduced in a gaseous state into the reaction vessel together with other source gases for providing the photoconductor layer 203. The IIIb atom-source compound or the Vb atom-source compound may preferably be gaseous compound under normal temperature and normal pressure, or at least a compound which can be readily gassifiable under the layer-forming condition.

[0411]

Specific examples of the IIIb atom-source compound may include: boron-source compounds, inclusive of boron hydrides, such as B_2H_6 , B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} , B_6H_{12} , and B_6H_{14} , and boron halides, such as BF_3 , BCl_3 , and

BBr_3 ; and further AlCl_3 , GaCl_3 , $\text{Ga}(\text{CH}_3)_3$, InCl_3 and TlCl_3 .

[0412]

Specific examples of the Bv atom-source compounds
5 may include: phosphorus-source compounds, inclusive of
boron hydrides, such as PH_3 and P_2H_4 , and phosphorus
halides, such as PH_4I , PF_3 , PF_5 , PCl_3 , PCl_5 , PBr_3 , PBr_5
and PI_3 ; and further AsH_3 , AsF_3 , AsCl_3 , AsBr_3 , AsF_5 ,
 SbH_3 , SbF_3 , SbF_5 , SbCl_3 , SbCl_5 , BiH_3 , BiCl_3 and BiBr_3 .
10 These conductivity-controlling atom-source compounds
may be diluted with H_2 and/or He as desired.

[0413]

It is also effective for the photoconductor layer
to contain carbon atom and/or oxygen atom and/or
15 nitrogen atom. The content(s) of the carbon and/or
oxygen and/or nitrogen may preferably be in a
proportion of 1×10^{-5} - 10 atm. %, more preferably 1×10^{-4} - 8 atm. %, further preferably 1×10^{-3} - 5 atm. %, based on the total of the silicon carbon oxygen and
20 nitrogen. The carbon and/or oxygen and/or nitrogen can
be contained at a uniform concentration throughout the
photoconductor layer 203 or at different concentrations
in a thickness direction of the photoconductor layer.

[0414]

25 The photoconductor layer 203 may have a thickness
determined appropriately depending on the desired
electrophotographic performances and economical

viewpoints, and preferably a thickness of 1 - 50 μm , more preferably 5 - 45 μm , further preferably 10 - 40 μm .

[0415]

5 During the formation of the photoconductor layer 203, the electroconductive support 201 may be held at an optimally set temperature, preferably 200 - 350 $^{\circ}\text{C}$, more preferably 230 - 330 $^{\circ}\text{C}$, further preferably 250 - 310 $^{\circ}\text{C}$.

10 [0416]

 The support temperature and gas pressure for producing the photoconductor layer 203 should not be determined independently but may desirably be determined in association with each other so as to
15 provide a photosensitive member having desired properties.

[0417]

 The photoconductor layer 203 formed on the electroconductive support 201 may preferably be coated
20 with a surface layer (surfacemost layer) 204 comprising a non-single crystal material. The surface layer 204 has a free surface and is disposed to provide improvements, principally in moisture-resistance performances in continuous and repetitive use,
25 electrical durability, environmental characteristic and durability.

[0418]

The surface layer 204 may comprise any non-single crystal material. For example, the surface layer may comprise: amorphous silicon containing hydrogen (H) and/or halogen (X) and further carbon (C) (denoted by
5 "a-SiC:H,X"), amorphous silicon containing hydrogen (H) and/or halogen (X) and further oxygen (O) (denoted by "a-SiO:H,X"), amorphous silicon containing hydrogen (H) and/or halogen (X) and further nitrogen (N) (denoted by "a-SiN:H,X"), and amorphous silicon containing hydrogen
10 (H) and/or halogen (X) and further at least one of carbon (C), oxygen (O) and nitrogen (N) (denoted by "a-SiCON:H,X").

[0419]

The surface layer 204 may be formed through
15 various vacuum film deposition processes, inclusive of glow discharge processes (AC-discharge CVD, such as low-frequency CVD, high-frequency CVD, and microwave CVD, or DC-discharge CVD), sputtering, vacuum evaporation, ion plating, photo-CVD, and thermo-CVD.
20 These vacuum film deposition processes and conditions thereof may be appropriately selected, in view of investment costs, production scale and desired properties of the resultant photosensitive members, but it is generally suitable to use a glow discharge
25 process, similar to the one for production of the photoconductor layer 203.

[0420]

For example, a surface layer 204 comprising a SiC:H,X may be produced according to the glow discharge process by introducing a silicon (Si)-source gas, a carbon (C)-source gas, a hydrogen (H)-source gas and/or
5 a halogen (X)-source gas into a reaction vessel placeable in a reduced pressure to cause flow discharge therein to form a layer of a-SiC:H,X on the photoconductor layer 203 already formed on an electroconductive support disposed in advance at a
10 prescribed position in the reaction vessel.
[0421]

In the surface layer 204 principally comprising SiC, the content of carbon may preferably be 30 - 90 atm. % based on the total of silicon and carbon atoms.
15 Particularly, by controlling the hydrogen content to 30 - 70 wt. % in the surface layer, it becomes possible to ensure a surface layer of a high hardness exhibiting remarkably improved electrical properties and high-speed continuous image forming performances.
20 [0422]

The hydrogen content in the surface layer can be controlled by controlling the H₂ gas flow rate, support temperature, discharge power, gas pressure, etc.
Further, the content(s) of hydrogen or/and halogen in
25 the surface layer may be controlled by controlling the support temperature, rates of introduction of hydrogen- and/or halogen-source gases, and discharge power, etc.

[0423]

The carbon, oxygen and/or nitrogen may be contained at constant concentrations throughout the surface layer or at different concentrations in a thickness direction of the surface layer.

[0424]

The surface layer 204 may preferably contain a conductivity-controlling atom at a concentration which may be constant throughout the surface layer or vary in a thickness direction of the surface layer 204.

[0425]

The conductivity-controlling atom may be a so-called impurity atom used in the semiconductor field, such as group IIb atom or group Vb atom, which may be introduced into the reaction in the form of a gaseous or gassifiable source-compound optionally diluted with a gas such as H₂, He, Ar or Ne.

[0426]

The surface layer 204 may preferably be formed in a thickness of 0.01 - 3 μm , more preferably 0.5 - 2 μm , further preferably 0.1 - 1 μm . If the thickness is below 0.01 μm , the surface layer is liable to be lost due to abrasion during the continual use of the photosensitive member, and above 3 μm , the electrophotographic performance of the photosensitive member is liable to be lowered, such as an increased residual potential.

[0427]

In order to form the surface layer 204 having desired properties to achieve the objects of the present invention, the temperature of the
5 electroconductive support 201 and gas pressure in the reaction vessel need to be set appropriately in accordance with the requirements.

[0428]

The conditions such as temperature of the support
10 and gas pressure to form the surface layer cannot be determined independently in normal cases, and it is desirable to determine the optimal values based on the mutual and organic association to form a photosensitive member having desired properties.

15 [0429]

It is effective to dispose between the photoconductor layer and the surface layer a buffer layer (lower surface layer) containing carbon, oxygen and/or nitrogen at a concentration lower than in the
20 surface layer for the purpose of improving the chargeability of the photosensitive member.

[0430]

Further, it is also possible dispose between the surface layer 204 and the photoconductive layer 203 a
25 thickness region wherein the concentration of carbon, oxygen and/or nitrogen is decreased toward the photoconductor layer 203. This is effective for

improving the adhesion between the surface layer and the photoconductor layer and reducing any interference caused by light reflection at the boundary.

[0431]

5 In the present invention, it is further preferred to use a surface layer comprising a non-single crystal carbon hydride film or an amorphous hydrogen-containing carbon film (denoted by "a-C:H").

[0432]

10 An a-C:H film also has a high hardness and is excellent in durability. An a-C:H film also has a low friction coefficient and shows excellent water repellency, so that it is possible to obviate image blurring in a high humidity environment without using a
15 heater for obviating the difficulty. Further, it is possible to prevent the attachment of electroconductive fine powder and other particles due to mechanical friction.

[0433]

20 In the present invention, the a-C:H surface layer may preferably contain a hydrogen content of 41 - 60 atm. %, more preferably 45 - 55 atm. % as calculated by $H/(C+H)$. If the hydrogen content is below 40 %, the resultant photosensitive member is liable to show an
25 insufficient sensitivity, thus being unsuitable for an image forming apparatus. Above 60 %, the fine texture of the film is liable to be impaired to result in a

weaker mechanical strength.

[0434]

The thickness of the surface layer of the image bearing member used in the present invention may be
5 optimally set in view of the wearing rate and the life of the image forming apparatus but may ordinarily be 0.01 - 10 μm , more preferably 0.1 - 1 μm . Below 0.01 μm , the mechanical strength can be impaired, and above 10 μm , the residual potential is liable to be
10 increased. The surface layer may suitably have a refractive index of ca. 1.8 - 2.8.

[0435]

The carbon-source compound may suitably comprise a gaseous or gassifiable hydrocarbon, such as CH_4 , C_2H_6 ,
15 C_3H_8 or C_4H_{10} . For easiness of handling and carbon supply efficiency at the time of layer formation, CH_4 and C_2H_6 are preferred. Such a carbon-source compound or gas may be diluted with another gas, such as H_2 , Ne, Ar or Ne before introduction to the reaction vessel.

20 [0436]

The substrate (electroconductive support) temperature may be adjusted in a range of from room temperature to 350 $^{\circ}\text{C}$. A rather low temperature may be preferred since too high a substrate temperature can
25 result in a film of a lower transparency because of a lowering in band gap. A higher rate of high-frequency power supply is generally preferred so as to

sufficiently decompose the hydrocarbon, more specifically at a rate of 5×10^{-6} J/(sec/m³) for the hydrocarbon gas feed, but as too high a power supply rate results in abnormal discharge to deteriorate the properties of the resultant image-bearing member, the power supply rate should be suppressed to a level of not causing abnormal discharge. The discharge space pressure may be held at a level of 1.33×10^{-2} - 1.33 kPa for a power supply of ordinary RF band (representatively 13.56 MHz, and 1.33×10^{-5} - 1.33×10^{-3} kPa for a power supply of VHF band (representatively 50 - 450 MHz).

[0437]

The a-C:H surface layer can further contain halogen atom as desired. Particularly, an amorphous carbonaceous film comprising principally carbon and also containing bonded fluorine inside or at the utmost surface of the film (denoted by an "a-C:H:F") layer may exhibit excellent water-repellency and low friction characteristic and can obviate image blurring in a high humidity environment without using a heater for obviating the difficulty.

[0438]

Such a halogen-containing surface layer may be produced in a similar manner as the a-C:H surface layer except for using a halogen-source gas. Examples of the halogen-source compound may include: F₂ and inter-

halogen compounds, such as BrF, ClF, ClF₃, BrF₃, BrF₅, IF₃ and IF₇. For the purpose of fluorine introduction, it is suitable to use a fluorine-containing gas, such as CF₄, CHF₃, C₂F₆, ClF₃, CHClF₂, F₂, C₃F₈ or C₄F₁₀.

5 [0439]

It is also suitable to dispose a layer of amorphous material between the photoconductor layer and the surface layer in order to improve the function of the image-bearing member. Such a layer may for example be
10 composed of non-single crystal silicon, non-single crystal silicon carbide, or non-single crystal carbon hydride.

[0440]

The photosensitive member used in the image
15 forming apparatus of the present invention may preferably include a charge injection-barrier layer between the electroconductive support and the photoconductor layer for preventing charge injection from the electroconductive support. More specifically,
20 the charge injection-barrier layer has a function of preventing charge injection from the support to the photoconductor layer when the photosensitive member is charged to a prescribed polarity on its free surface but does not show such a function when the
25 photosensitive member free surface is charged to an opposite polarity, thus showing a so-called polarity-dependence. For imparting such a function, the charge

injection barrier layer is caused to contain a relatively large amount of conductivity-controlling atom compared with the photoconductor layer.

[0441]

5 The conductivity-controlling atom can be contained in the charge injection-barrier layer at a constant concentration or at different concentrations with a certain concentration distribution. In the case of different concentrations, it is preferred that the
10 conductivity-controlling atom is present at a higher concentration in proximity to the support. In any case, it is preferred that the controlling atom is present at a constant concentration in a plane parallel to the substrate surface so as to uniformize the
15 performance in a planar direction.

[0442]

 The conductivity-controlling atom contained in the charge injection barrier layer may be a so-called impurity atom used in the semiconductor field, such as
20 group IIIb atom or group Vb atom.

[0443]

 The charge injection barrier layer may preferably be formed in a thickness of 0.1 - 5 μm , more preferably 0.3 - 4 μm , further preferably 0.5 - 3 μm .

25 [0444]

 In the present invention, the ranges described above may be selected as the desirable numerical range

for conditions inclusive of diluted gas mixture ratio, gas pressure, discharge power and support temperature to form the charge injection barrier layer. These factors to form the layer cannot be determined
5 independently in normal cases, and it is desirable to determine the optimum values of each layer formation factor based on the mutual and organic association to form a surface layer having desired properties.
[0445]

10 In order to provide a further improved adhesion between the electroconductive support 201 and the photoconductor layer 203 or the charge injection barrier layer 202, it is possible to insert an adhesive layer formed of an amorphous material principally
15 comprising Si_3N_4 , SiO_2 or silicon atom and further containing hydrogen and/or halogen, and carbon and/or oxygen and/or nitrogen. Further, in order to prevent the occurrence of interference fringes due to reflection light from the support, it is possible to
20 dispose a light-absorbing layer.
[0446]

Hereinafter, the apparatus and method of producing the photosensitive member to be used in the present invention will be described more specifically. Fig. 7
25 schematically shows an example of a deposition device of the image-bearing member by the RF plasma CVD method using high-frequency power source.

[0447]

This device roughly comprises the deposition device 2100, a gas supply unit 2200 for supplying material gas, and an exhaust unit (not shown) for
5 reducing pressure in a reaction vessel 2110. In the reaction vessel 2110 in the deposition device 2100, an electroconductive support 2112 as a cylindrical coated substrate connected to a ground, a heater 2113 for heating the electroconductive support, and a gas
10 introduction pipe 2114 for introducing material gas are provided, and the high-frequency power source 2110 is further connected via a high-frequency matching box 2115.

[0448]

15 The material gas supply unit 2200 comprises material gas cylinders 2221 to 2226, valves 2231 to 2236, inflow valves 2241 to 2246, outflow valves 2251 to 2256, and mass-flow controllers 2211 to 2216 for SiH_4 , H_2 , CH_4 , NO , B_2H_6 , CF_4 , etc., and each gas cylinder
20 is connected to the gas introduction pipe 2114 in the reaction vessel 2110 via an auxiliary valve 2260.

[0449]

The electroconductive support 2112 is connected to the ground by providing on an electroconductive
25 platform 2123.

[0450]

Hereinafter an example of a procedure for forming

an image-bearing member using the device shown in Fig. 7 will be described.

[0451]

5 The electroconductive support 2112 is provided in the reaction vessel 2110 and air in the reaction vessel 2110 is discharged using the exhaust unit not shown (e.g., vacuum pump). Then, the temperature of the electroconductive support 2112 is controlled at a desired temperature between 20 - 500 °C using the
10 heater 2113. Next, material gas for forming the image-bearing member is flown into the reaction chamber 2110. When flowing in material gas, closing of the gas cylinder valves 2231 to 2236 and a leak valve 2117 of the reaction vessel is verified, as well as opening of
15 the inflow valves 2241 to 2246, the outflow valves 2251 to 2256, and the auxiliary valve 2260 is verified, and then air in the reaction vessel 2110 and the gas pipe 2116 is discharged by opening the main valve 2118.

[0452]

20 After that, at the moment when the reading of the vacuum gauge 2119 is 0.67 mPa, the auxiliary valve 2260 and the outflow valves 2251 to 2256 are closed. Then, the individual gasses are introduced by opening the valves 2231 to 2236 from the material gas cylinders
25 2221 to 2226 and each gas pressure is adjusted to 196 kPa using the pressure adjusters 2261 to 2266. Next, the inflow valves 2241 to 2246 are gradually opened and

thereby introducing the individual gasses into the mass-flow controllers 2211 to 2216.

[0453]

Once the preparation has been completed following
5 the above-mentioned procedure, a photosensitive layer is formed on the electroconductive support 2112 from the electroconductive support 2112 side, namely from the lower layer in turn. Now, the formation of a photoconductive layer will be described.

10 [0454]

When the electroconductive support 2112 has the desired temperature, necessary outflow valves 2251 to 2256 and the auxiliary valve 2260 are opened gradually to introduce desired material gasses from the gas
15 cylinders 2221 to 2226 into the reaction vessel 2110 via the gas introduction pipe 2114. Then, using the mass-flow controllers 2211 to 2216, the flow rate of each material gas is adjusted to the desired value. At that time, opening of the main valve 2118 is adjusted
20 while observing the vacuum gauge 2119 so that the pressure inside the reaction vessel is the desired value of 133.3 Pa or less.

[0455]

After the internal pressure is stabilized, by
25 setting the high-frequency power source 2120 at the desired power, for example, frequency of 1 - 450 MHz, and more specifically, for example, high-frequency

power of 13.56 MHz is supplied to the cathode electrode 2111 via the high-frequency matching box 2115 to generate high-frequency glow discharge. This discharge energy dissolve the material gasses introduced into the reaction vessel 2110 and a photoconductive layer having a desired silicon atom as a main component is deposited on the electroconductive support 2112. After the film with a desired thickness has been formed, supply of high-frequency power is stopped, and inflow of material gasses into the reaction vessel 2110 is turned off by closing the applicable outflow valves 2251 to 2256 to complete the formation of the photoconductive layer.

[0456]

For formation of the photoconductive layer and film thickness, well-known information can be used.

When a surface layer is formed on the above-mentioned photoconductive layer, the above operations may be repeated in principle.

[0457]

Fig. 8 schematically shows an example of the deposition device of the image-bearing member by the VHF plasma CVD method using the VHF power source. This device is constructed by replacing the deposition device 2100 shown in Fig. 7 with the deposition device 3100 in Fig. 8.

[0458]

The deposition film in this device by the VHF

plasma CVD method can be formed in accordance with the following procedure.

[0459]

First of all, the electroconductive support 3112
5 is provided in the reaction vessel 3111. The
electroconductive support 3112 is rotated by the
driving unit 3120. Air in the reaction vessel 3111 is
discharged using an exhaust unit not shown (e.g.,
diffusion pump) via the exhaust pipe 3121 and the
10 pressure inside the reaction vessel 3111 is adjusted to
 1.33×10^{-5} Pa or less. Then, the temperature of the
electroconductive support 3112 is heated and retained
to the specified temperature between 50 and 500 °C
using the heater 3113.

15 [0460]

In order to inflow material gasses for forming a
deposition layer into the reaction vessel 3111, closing
of the gas cylinder valves and leak valve (not shown)
of the reaction vessel is verified, as well as opening
20 of the inflow valves, the outflow valves and the
auxiliary is verified. Then, firstly the main valve
(not shown) is opened to exhaust inside the reaction
vessel 3111 and the gas pipes.

[0461]

25 At the moment when the reading of the pressure
gauge (not shown) is 6.65×10^{-4} Pa, the auxiliary
valve and the outflow valves are closed.

[0462]

Then, gasses are introduced by opening the valves of the cylinders from the gas cylinders and each gas pressure is adjusted to 2×10^5 Pa using the pressure
5 adjustor. Next, the inflow valves are opened gradually to introduce gasses into the mass-flow controllers.

[0463]

After the preparation for forming a film has been completed in this way, a deposition film is formed on
10 the electroconductive support 3112 in accordance with the following procedure.

[0464]

When the temperature of the electroconductive support (3112) is at the specified value, necessary
15 outflow valves and the auxiliary valve are opened gradually and the specified gasses are introduced into the discharge space 3130 in the reaction vessel 3111 via the gas introduction pipe (not shown) from the gas cylinders. Next, the flow rate of each material gas is
20 adjusted by the mass-flow controller to the specified value. At that time, the opening of the main valve (not shown) is adjusted while observing the vacuum gauge (not shown) so that the pressure in the discharge space 3130 is at the specified value of 133 Pa or
25 lower.

[0465]

Once the pressure is stabilized, the VHF power

source (not shown) of 50 - 450 MHz, for example, with frequency of 105 MHz at the desired power, and VHF power is introduced into the discharge space 3130 via the matching box 3116 to generate glow discharge. Now,
5 in the discharge space 3130 surrounded by the electroconductive support 3112, material gas introduced is excited and dissociated by the discharge energy and a specified deposition film is formed on the electroconductive support 3112. At this time, at the
10 same time of introduction of VHF power, output of heater 3113 is adjusted and the temperature of the electroconductive support is varied at the specified value. At this time, in order to uniformize the layer formation, rotation is made at the desired rotation
15 speed using the driving unit 3120.

[0466]

After the formation of the film with the desired thickness, supply of VHF power is stopped and inflow of gas into the reaction vessel is turned off by closing
20 the outflow valve to complete the formation of the deposition film.

By repeating these operations several times, the image-bearing member having the desired multi-layer structure can be formed.

25 [0467]

In forming individual layers, there is no need to say that all the outflow valves, except for necessary

valves, are closed. In order to prevent gasses from remaining in the reaction vessel 3111 and any pipe from the outflow valve to the reaction vessel 3111, the operations to exhaust in the system to high vacuum by
5 closing the outflow valves, opening the auxiliary valve, and completely opening the main valve (not shown) should be conducted as needed.

[0468]

There is no need to say that above-mentioned gas
10 types and valve operations can be changed in accordance with the preparation conditions of individual layers.

[0469]

In the image forming method of the present invention, the image-bearing member (photosensitive
15 member) is primarily charged by a contact charging member to a potential of 250 to 600 volts in terms of an absolute value. If the potential on the image-bearing member is below 250 volts, it becomes difficult to take a balance between the image part density and
20 fog at the background part. On the other hand, in excess of 600 volts, an increased current is required to charge the image-bearing member to such a primary potential level, and image defects due to charge leakage is liable to occur corresponding thereto. For
25 a similar reason, a potential of 250 to 500 volts is further preferred. The polarity (positive or negative) of the primary charge potential may be appropriately be

determined in harmony with process steps of developing, charging, electrostatic latent image formation, and transfer of the image forming system (method and apparatus).

5 [0470]

The image forming apparatus of the present invention may preferably be free from means for directly warming the image-bearing member, e.g., for minimizing power consumption, but it is not prevented
10 to provide such a warming means as desired.

[0471]

In the latent image forming step of the image forming method according to the present invention, the charged surface of the image-bearing member may be
15 exposed to imagewise exposure light carrying given image data preferably emitted from an imagewise exposure means to form an electrostatic latent image on the charged surface of the image-bearing member.

[0472]

20 The imagewise exposure means is not limited to a laser scanning exposure means suitable for digital latent image formation but can be ordinary analog imagewise exposure means or other light-emitting devices, such as LED, or a combination of light source,
25 such as fluorescent lamp, and a liquid crystal shutter, as long as it can form a electrostatic latent image corresponding to the image information.

[0473]

The image-bearing member may be a electrostatic latent image recording dielectric material or the like. In this case, after primary charging the surface of the dielectric material uniformly to the specified polarity and potential, electricity is eliminated selectively using the means for eliminating electricity such as eliminating needle head and electron gun to form by writing a targeted electrostatic latent image.

10 [0474]

Next, a developing step will be described. In the developing step of the image forming method according to the present invention, an electrostatic latent image on the image-bearing member is developed with the toner of the present invention carried on a toner-carrying member. First of all, the toner-carrying member to be used for development will be described.

[0475]

The toner-carrying member may preferably comprise an electroconductive cylinder (developing roller) formed of a metal or alloy, such as aluminum or stainless steel. It is also possible to form such an electroconductive cylinder with a resin composition having sufficient mechanical strength and electroconductivity, or use an electroconductive rubber roller. Instead of such a cylindrical member, it is also possible to use an endless belt which can be

driven in rotation.

[0476]

In the present invention, it is preferred to form a toner layer at a coating rate of 5 - 50 g/m² on the
5 toner-carrying member. If the toner coating rate is below 5 g/m², it becomes difficult to attain a sufficient image density and the toner layer irregularity is liable to occur due to an excessive charge of the toner. If the toner coating rate is
10 above 50 g/m², toner scattering is liable to occur.

[0477]

The toner-carrying member used in the present invention may preferably have a surface roughness (in terms of JIS center line-average surface roughness
15 (Ra)) in the range of 0.2 - 3.5 μm.

If Ra is below 0.2 μm, the toner on the toner-carrying member is liable to be charged excessively to have an insufficient developing performance. If Ra exceeds 3.5 μm, the toner coating layer on the toner-
20 carrying member is liable to be accompanied with irregularities, thus resulting images with density irregularity. Ra is further preferably in the range of 0.5 - 3.0 μm.

[0478]

25 In the present invention, the surface roughness (Ra) values described herein are based on values measured as center line-average roughness values by

using a surface roughness meter ("Surfcorder SE-30H", available from K.K. Kosaka Kenkyusho) according to JIS B-0601. More specifically, based on a surface roughness curve obtained for a sample surface, a length
5 of a is taken along a center line of the roughness curve. The roughness curve is represented by a function $Y = f(x)$ while setting the X-axis on the center line and a roughness scale (y) on the Y-axis along the length x portion. A center line-average
10 roughness R_a of the roughness curve is determined by the following formula.

[0479]

As the toner of the present invention has a high chargeability, it is desirable to control the total
15 charge thereof for use in actual development, so that the toner-carrying member used in the present invention may preferably be surfaced with a resin layer containing electroconductive fine particles and/or lubricating particles dispersed therein.

20 [0480]

The electroconductive fine particles dispersed in the coating resin layer of the toner-carrying member may preferably exhibit a resistivity of at most 0.5 ohm.cm as measured under a pressure of 120 kg/cm².

25 The electroconductive fine particles may preferably comprise carbon fine particles, crystalline graphite particles or a mixture of these, and may

preferably have a particle size of 0.005 - 10 μm .

[0481]

Examples of the resin constituting the surface layer of the developer-carrying member may include:

5 thermoplastic resin, such as styrene resin, vinyl resin
polyethersulfone resin, polycarbonate resin,
polyphenylene oxide resin, polyamide resin, fluorine-
containing resin, cellulose resin, and acrylic resin;
thermosetting resins, such as epoxy resin, polyester
10 resin, alkyd resin, phenolic resin, urea resin,
silicone resin and polyimide resin; thermosetting
resins.

[0482]

Among the above, it is preferred to use a resin
15 showing a releasability, such as silicone resin or
fluorine-containing resin; or a resin having excellent
mechanical properties, such as polyethersulfone,
polycarbonate, polyphenylene oxide, polyamide, phenolic
resin, polyester, polyurethane resin or styrene resin.
20 Phenolic resin is particularly preferred.

[0483]

The electroconductive fine particles may
preferably be used in 3 - 20 wt. parts per 10 wt. parts
of the resin. In the case of using a mixture of carbon
25 particles and graphite particles, the carbon particles
may preferably be used in 1 to 50 wt. parts per 10 wt.
parts of the graphite particles. The coating layer

containing the electro-conductive fine particles of the toner-carrying member may preferably have a volume resistivity of 10^{-6} to 10^6 ohm.cm, more preferably 10^{-1} to 10^6 ohm.cm.

5 [0484]

In the present invention, it is preferred that the toner on the toner-carrying member is regulated by a ferromagnetic metal blade 11a disposed opposite to an with a small gap from the toner-carrying member, so as
10 to stably retain the powder characteristic and chargeability of the toner for a long period, thereby providing a toner with a uniform charge not liable to cause toner scattering without being affected by environmental conditions such as temperature and
15 humidity.

[0485]

In the image forming method of the present invention, the toner-carrying member may preferably be moved with a speed difference relative to the image-
20 bearing member surface speed so as to sufficiently supply the toner particles and electroconductive fine powder from the toner-carrying member to the image-bearing member side, thereby providing good images.

[0486]

25 The toner-carrying member surface may be moved in a direction which is identical to or opposite to the moving direction of the image-bearing member surface at

the developing section. In the case of movement in the identical direction, the toner-carrying member may preferably be moved at a surface velocity which is at least 100 % of that of the image-bearing member. Below
5 100 %, the image quality can be lowered in some cases.
[0487]

A higher surface speed ratio supplies a larger amount of toner to the developing section, thus increasing the frequency of attachment onto and
10 returning from the latent image on the image-bearing member of the toner, i.e., more frequent repetition of removal from an unnecessary part and attachment onto a necessary part of the toner, to provide a toner image more faithful to a latent image. The speed ratio can
15 be calculated according to the following formula:
[Mathematical Formula 5]

Speed ratio (%)
= {(toner-carrying member surface speed)/
(image-bearing member surface speed)} x 100.
20 [0488]

A surface speed ratio of 105 - 300 % between the toner-carrying member and the image-bearing member is further preferred.
[0489]

25 In the present invention, in order to apply the non-contact developing method, it is preferable to form a toner layer on the toner-carrying member thinner than

the gap distance between the toner-carrying member and the image-bearing member. The development step is effected in a state of no contact between the toner layer on the toner-carrying member and the
5 photosensitive member (image-bearing member) in the developing region. As a result, it is possible to obviate development fog caused by injection of the developing bias voltage to the image-bearing member even if electroconductive fine powder having a low
10 resistivity is added into the toner, thus being able to obtain good images.

[0490]

In the image forming method of the present invention, in order to obtain fog-free high-quality
15 images, it is preferable to apply the magnetic toner in a layer thickness, which is smaller than the closest gap (between S and D) between the toner-carrying member and the image-bearing member (e.g., photosensitive member) on the toner-carrying member and effect the
20 development under application of an alternating voltage. More specifically, the closest gap between the photosensitive member and the toner-carrying member is wider than the toner layer thickness on the toner-carrying member by the layer pressure-regulating member
25 for regulating the magnetic toner on the toner-carrying member. But the toner on the toner-carrying member is regulated using the ferromagnetic metal blade whose

layer thickness-regulating member for regulating the magnetic toner on the toner-carrying member is disposed opposite to the toner-carrying member with a minute gap. This is especially preferable from the viewpoints
5 of maintaining the powder characteristics and charging features for a long period of time, and realizing uniform charging which is hard to be influenced by environment such as humidity and temperature and hard to cause toner fly out.

10 [0491]

it is preferred that the toner-carrying member is disposed with a spacing of 100 - 1000 μm , more preferably 120 - 500 μm , from the image-bearing member. If the spacing is below 100 μm , the developing
15 performance with the toner is liable to be fluctuated depending on a fluctuation of the spacing, so that it becomes difficult to mass-produce image-forming apparatus satisfying stable image qualities. If the spacing exceeds 1000 μm , the followability of toner
20 onto the latent image on the image-bearing member is lowered, thus being liable to cause image quality lowering, such as lower resolution and lower image density.

[0492]

25 In the present invention, it is preferred to operate the developing step under application of an alternating electric field (AC electric field) between

the toner-carrying member and the image-bearing member. The alternating developing bias voltage may be a superposition of a DC voltage with an alternating voltage (AC voltage).

5 [0493]

The alternating bias voltage may have a waveform which may be a sine wave, a rectangular wave, a triangular wave, etc., as appropriately be selected. It is also possible to use pulse voltages formed by periodically turning on and off a DC power supply. Thus, it is possible to use an alternating voltage waveform having periodically changing voltage values.

10 [0494]

It is preferred to form an AC electric field at a peak-to-peak intensity of 3×10^6 - 10×10^6 V/m and a frequency of 100 to 5000 Hz between the toner-carrying member and the image-bearing member by applying a developing bias voltage.

15 [0495]

20 If the AC electric field strength is below 3×10^6 V/m, the performance of recovery of transfer-residual toner is lowered, thus being liable to result in foggy images. Further, because of a lower developing ability, images having a lower density are liable to be formed. On the other hand, if the AC electric field exceeds 1×10^7 V/m, too large a developing ability is

25 liable to result in a lower resolution because of

collapsing of thin lines and image quality
deterioration due to increased fog, a lowering in
chargeability of the image-bearing member and image
defects due to leakage of the developing bias voltage
5 to the image-bearing member.

[0496]

If the frequency of the AC electric field is below
100 Hz, the frequency of toner attachment onto and
toner removal from the latent image is lowered and the
10 recovery of transfer-residual toner is liable to be
lowered, thus being liable to result in a lower
developing performance. If the frequency exceeds 5000
Hz, the amount of toner following the electric field
change is lowered, thus being liable to result in a
15 lowering in transfer-residual toner recovery and a
lowering in developing performance.

[0497]

By applying an alternating electric field as a
developing bias voltage, charge injection to the image-
20 bearing member at the developing section is prevented
even if a high potential difference is present between
the toner-carrying member and the image-bearing member,
so that the electroconductive fine powder added in the
toner on the toner-carrying member can be evenly
25 transferred onto the image bearing member, thereby
promoting the uniform contact and charging in the
charging section.

[0498]

Next, a contact transfer step preferably adopted in the image forming method of the present invention will now be described. The transfer step of the present invention can be step of once transferring the toner image formed in the developing step to an intermediate transfer member and then re-transferring the toner image onto a recording medium, such as paper. Thus, the transfer material receiving the transfer of the toner image from the image-bearing member can be an intermediate transfer member, such as a transfer drum.

[0499]

In the present invention, it is preferred to adopt a contact transfer step wherein a toner image on the image-bearing member is transferred onto a transfer(-receiving) material while abutting a transfer(-promoting) member against the image-bearing member via the transfer material, and the abutting pressure of the transfer member may preferably be a linear pressure of at least 2.9 N/m (3 g/cm), more preferably at least 19.6 N/m (20 g/cm). If the abutting pressure is below 2.9 N/m, difficulties, such as deviation in conveyance of the transfer material and transfer failure, are liable to occur.

[0500]

The transfer member used in the contact transfer step may preferably be a transfer roller as illustrated

in Fig. 9 or a transfer belt. Referring to Fig. 9, a transfer roller 34 may comprise a core metal 34a and a conductive elastic layer 34b coating the core metal 34a. The conductive elastic layer 34b may comprise an
5 elastic material, such as polyurethane rubber or ethylene-propylene-diene rubber (EPDM), and an electroconductivity-imparting agent, such as carbon black, dispersed in the elastic material so as to provide a medium level of electrical resistivity
10 (volume resistivity of $10^6 - 10^{10}$ ohm.cm. The transfer roller is supplied with a transfer bias voltage from a transfer bias voltage supply 35.

[0501]

Next, an image forming method including a
15 developing-cleaning step (cleanerless system) as an embodiment of the present invention will be described.

Fig. 3 schematically illustrates an embodiment of image forming apparatus including a charging roller for the injection charging scheme.

20 [0502]

A cleaning unit including a cleaning member, such as a cleaning blade has been removed from the image forming apparatus, and a layer of the above-mentioned specific magnetic toner(mono-component toner) carried
25 on a toner-carrying member is used to develop a latent image on an image-bearing member while being in non-contact with the image-bearing member.

[0503]

The image forming system includes a rotating drum-type a-Si image-bearing member 1 which is driven in rotation in an indicated arrow direction at a constant
5 peripheral speed (process speed).

[0504]

A charging roller 306 as a contact charging member is abutted against the image-bearing member 1 at a prescribed pressing force in resistance to its
10 elasticity so as to form a charging contact nip between the image-bearing member 1 and the charging roller 306. The charging roller 306 is driven in rotation in a counterdirection with respect to the image-bearing member (i.e., so as to provide a surface moving
15 direction opposite to that of the image-bearing member) at the charging nip, thus providing a surface speed difference between the image-bearing member 1 and the charging roller 306. The above-mentioned electroconductive fine powder is applied at a uniform
20 coating rate on the surface of the charging roller 306.

[0505]

The charging roller 306 is provided with a core metal (not shown) to which a DC charging bias voltage is applied from a charging bias voltage supply (not
25 shown). As a result, the image-bearing member 1 surface is uniformly charged to a potential which is almost identical to the DC bias voltage applied to the

charging roller 306 according to the direct injection charging scheme.

[0506]

5 The thus-charged image-bearing member 1 surface is then exposed to laser light L carrying objective image data to form an electrostatic image thereon, which is then developed as a toner image by a developing device 307.

[0507]

10 The developing device 307 is a non-contact reversal developing device having a structure as shown in Fig. 4, and includes a developing sleeve (toner-carrying member) 1 rotated in an arrow direction so as to provide a prescribed spherical speed in a surface moving direction identical to that of the image-bearing member 1 at a developing section which is a region where the image-bearing member 1 and the developing sleeve 12 are opposite to each other. Under the action of a magnetic field formed between the magnetic blade 11a, the magnetic toner is charged and applied in the thin layer 13 at a regulated thickness. The layer 13 of magnetic toner formed on the developing sleeve 12 is brought to the developing section opposite to the image-bearing member 1, where the magnetic toner is caused to jump onto the electrostatic latent image on the image-bearing member 1 under the action of a developing bias voltage applied to the developing

15

20

25

sleeve 12 from a bias voltage supply, thereby forming a toner image on the image-bearing member 1 (mono-component jumping development).

[0508]

5 A transfer roller 302 as a contact transfer means is abutted against the image-bearing member 1 at a prescribed linear pressure to form a transfer nip, where a transfer material P is supplied via conveyer rollers 308a and 308b and guides 309a and 309b at a
10 prescribed timing, i.e., in synchronism with the toner image formation on the image-bearing member 1, whereby the toner image on the image-bearing member 1 is successively transferred onto a surface of the transfer material P under the action of a prescribed transfer
15 bias voltage applied to the transfer roller 302 from a transfer bias voltage supply (not shown). The transfer roller 302 is designed to have a prescribed resistance value and supplied with a DC voltage to effect the transfer. The transfer material conveyed to the
20 transfer nip is conveyed through the nip while receiving the toner image on the image-bearing member 1 under the action of an electrostatic force and a pressing force.

[0509]

25 The transfer material P having received the toner image at the transfer section is then separated from the image-bearing member 1 and conveyed via a guide 311

to a heat-fixation type fixing device 313, where the toner image is fixed onto the transfer material to form an image product (print or copy), which is then discharged out of the apparatus.

5 [0510]

A cleaning unit 312 as included in the apparatus of Fig. 2 has been removed from the apparatus of Fig. 3. As a result, transfer residual toner remaining on the image-bearing member 1 after the toner image transfer onto the transfer material is not removed by such a cleaning unit, and along with the rotation of the image-bearing member 1, is conveyed via the charging section to reach the developing section, where the residual toner is subjected to a developing-cleaning operation to be recovered thereat.

[0511]

Now, the behavior or movement of the electroconductive fine powder in the above-mentioned cleanerless image forming system will be described.

20 [0512]

Electroconductive fine powder mixed in the magnetic toner T in the developing device 307 is moved together with the toner and transferred in an appropriate amount to the photosensitive member (image-bearing member) 1 at the time of developing operation of the developing device 307.

[0513]

The toner image (composed of toner particles) on the photosensitive member 1 is positively transferred onto the transfer material P (recording medium) under an influence of a transfer bias voltage at the transfer section. However, because of its electroconductivity, the electroconductive fine powder on the photosensitive member 1 is not positively transferred to the transfer material P but substantially remains in attachment onto the photosensitive member 1.

10 [0514]

As no cleaning unit is involved in the image forming apparatus of Fig. 3, the transfer-residual toner particles and the electroconductive fine powder remaining on the photosensitive member 1 after the transfer step are, along with the rotation of the photosensitive member 1, brought to the charging section formed at the contact part between the photosensitive member 1 and the charging roller 306 (contact charging member) to be attached to and mixed with the charging roller 306. As a result, the photosensitive member 1 is charged by direct charge injection in the presence of the electroconductive fine powder at the contact part between the photosensitive member 1 and the charging roller 306.

25 [0515]

By the presence of the electroconductive fine powder, the intimate contact and low contact

resistivity between the charging roller 306 and the photosensitive member 1 can be maintained even when the transfer-residual toner particles are attached to the charging roller 306, thereby allowing the direct
5 injection charging of the photosensitive member 1 by the charging roller 306.

[0516]

More specifically, the charging roller 306 intimately contacts the photosensitive member 1 via the
10 electroconductive fine powder, and the electroconductive fine powder rubs the photosensitive member 1 surface without discontinuity. As a result, the charging of the photosensitive member 1 by the charging roller 306 is performed not relying on the
15 discharge charging mechanism but predominantly relying on the stable and safe direct injection charging mechanism, to realize a high charging efficiency that has not been realized by conventional roller charging. As a result, a potential almost identical to the
20 voltage applied to the charging roller 306 can be imparted to the photosensitive member 1.

[0517]

The transfer-residual toner attached to the charging roller 306 is gradually discharged or released
25 from the charging roller 306 to the photosensitive member 1, and along with the movement of the photosensitive member 1, reaches the developing section

where the residual toner is recovered to the developing device 307 in the developing-cleaning operation.

[0518]

The developing-cleaning step is a step of
5 receiving the toner remaining on the photosensitive member 1 after the transfer step at the time of developing operation in a subsequent cycle of image formation (developing of a latent image formed by re-charging and exposure after a previous image forming
10 cycle operation having resulted in the transfer-residual toner particles) under the action of a fog-removing bias voltage of the developing device (V_{back} , i.e., a difference between a DC voltage applied to the developing device and a surface potential on the
15 photosensitive member). In an image forming apparatus adopting a reversal development scheme adopted in this embodiment, the developing-cleaning operation is effected under the action of an electric field of recovering toner particles from a dark-potential part
20 on the photosensitive member and an electric field of attaching toner particles from the developing sleeve and a light-potential part on the photosensitive member, respectively, exerted by the developing bias voltage.

25 [0519]

As the image-forming apparatus is operated, the electroconductive fine powder contained in the magnetic

toner T in the developing device 307 is transferred to the photosensitive member 1 surface at the developing section, and moved via the transfer section to the charging section along with the movement of the
5 photosensitive member 1 surface, whereby the charging section is successively supplied with fresh electroconductive fine powder. As a result, even when the electroconductive fine powder is reduced by falling, etc., or the electroconductive fine powder at
10 the charging section is deteriorated, the chargeability of the photosensitive member 1 at the charging section is prevented from being lowered and good chargeability of the photosensitive member 1 is stably retained.

[0520]

15 In this way, in the image forming apparatus including a contact charging scheme, a transfer scheme and a toner recycle scheme, the photosensitive member 1 (as an image-bearing member) can be uniformly charged at a low application voltage by using a simple charging
20 roller 306. Further, the direct injection charging of the ozonless-type can be stably retained to exhibit uniform charging performance even through the charging roller 306 is soiled with transfer-residual toner particles. As a result, it is possible to provide an
25 inexpensive image forming apparatus of a simple structure free from difficulties, such as generation of ozone products and charging failure.

[0521]

As mentioned above, it is necessary for the electroconductive fine powder to have a resistivity of at most 1×10^9 ohm.cm for not impairing the charging performance. As a result, in a developing device wherein a magnetic toner directly contacts an image-bearing member 1, charges are injected to the image-bearing member 1 via the electroconductive fine powder in the toner under the application of a developing bias voltage, causing a fog.

[0522]

However, a non-contact developing device is used in this embodiment, so that good images can be formed without causing charge injection to the photosensitive member by the developing bias voltage. Further, as the charge injection to the photosensitive member is not caused at the developing section, it is possible to provide a high potential difference between the development sleeve 12 and the photosensitive member 1 (19) as by application of an AC bias voltage. As a result, it becomes possible to uniformly develop the electroconductive fine powder onto the photosensitive member 1 surface to achieve uniform contact at the charging section to effect the uniform charging, thereby obtaining good image.

[0523]

Owing to the lubricating effect (friction-reducing

effect) of the electroconductive fine powder present at the contact part between the charging roller 306 and the photosensitive member 1, it becomes possible to easily and effectively provide a speed difference
5 between the charging roller 306 and the photosensitive member 1. Owing to the lubricating effect, the friction between the charging roller 306 and the photosensitive member 1 is reduced, the drive torque is reduced, and the surface abrasion or damage of the
10 charging roller 306 and the photosensitive member 1 can be reduced. As a result of the speed difference, it becomes possible to remarkably increase the opportunity of the electroconductive fine powder contacting the photosensitive member 1 at the contact part (charging
15 section) n between the charging roller 306 and the photosensitive member 1, thereby allowing good direct injection charging.

[0524]

In this embodiment, the charging roller 306 is
20 driven in rotation to provide a surface moving direction which is opposite to that of the photosensitive member 1 surface at the charging section n, whereby the transfer-residual toner particles on the photosensitive member 1 brought to the charging section
25 are once recovered by the charging roller 1 to level the density of the transfer-residual toner particles present at the charging section. As a result, it

becomes possible to prevent charging failure due to localization of the transfer-residual toner particles at the charging section, thereby achieving stabler charging performance.

5 [0525]

Furthermore, in this embodiment, due to the presence of adequate amount of electroconductive fine powders at the charging contact position with the charging roller 306 as a contact charging member with
10 the image-bearing member 1, it is easy to reduce frictions between the charging roller 306 and the image-bearing member 1 due to the lubrication effect of the particles and rotary drive the charging roller 306 with speed difference from the image-bearing member.
15 In other words, it is possible to reduce the driving torque and prevent abrasion or scarring on the surfaces of the charging roller 306 and the image-bearing member 1. It is also possible to realize sufficient charging performance due to increased contact opportunities by
20 the particles. There is no negative influence on image formation due to coming off of the electroconductive fine powder from the charging roller 306.

[0526]

The image forming apparatus of the present
25 invention may have the structure including a means to realize the steps of the image forming method described above, thus being able to use the means such as an

apparatus conventionally known.

[0527]

The measurement methods of various property data related to the present invention will be described in
5 detail.

(1) Measurement method of fog of fixed images

Fog was measured by a reflectometer ("MODEL TC-6DS", made by Tokyo Denshoku K.K.).

A green filter was used and the fog was calculated
10 from the following formula. The smaller value means less amount of fog.

[Mathematical Formula 6]

Fog (reflectance) (%)

= Reflectance on a standard paper (%) -

15 Reflectance of a sample non-image portion (%)

[0528]

(2) Primary charging potential of the image-bearing member

An image-bearing member incorporated in an image
20 forming apparatus is primarily charged by a prescribed charger and a charged position is moved to a point closest to a developing sleeve of a developing device, where the surface potential is measured at three point along a generatrix of the image-bearing member, i.e.,
25 at 2 points at distances of 50 mm \pm 10 mm toward the center from both ends and at 1 point of \pm 10 mm from the center by a non-contact potentiometer ("Model 344",

available from T Rek K.K.). An average of the three measured values is recorded as a measured primary charging voltage.

[0529]

5 [Examples]

Hereinbelow, the present invention will be described more specifically based on Examples which however should not be construed to restrict the scope of the present invention.

10 [0530]

<Surface-treated magnetic powder 1>

Into a ferrous sulfate aqueous solution, a caustic soda solution in an amount of 1.0 - 1.1 equivalent of the ferrous ion was added and mixed to
15 prepare an aqueous solution containing ferrous hydroxide

[0531]

While maintaining the pH at ca. 9, air was blown into the aqueous solution to cause oxidation at 80 - 90
20 °C, thereby forming a slurry containing seed crystals.

[0532]

Then, into the slurry, a ferrous sulfate aqueous solution in an amount of 0.9 - 1.2 equivalent of the alkali (i.e., sodium in the caustic soda solution) was
25 added, and while maintaining the pH of the slurry at 8, air was blown into the slurry to proceed with oxidation. After the oxidation, the resultant magnetic

iron oxide powder was washed and once recovered by filtration. A small portion of the wet sample was sampled to measure the moisture content. Then, the wet sample (without drying) was re-dispersed in a separate aqueous medium, and the pH of the dispersion liquid was adjusted to ca. 6. Then, into the dispersion liquid under sufficient stirring, a silane coupling agent ($n\text{-C}_{10}\text{H}_{21}\text{Si}(\text{OCH}_3)_3$) in an amount of 1.9 wt. parts of the magnetic iron oxide (of which the amount was measured in advance by subtracting the moisture content from the wet magnetic iron oxide weight) was added to effect a coupling treatment. The resultant hydrophobic iron oxide powder was washed, filtered out and dried in an ordinary manner, followed by disintegration of slight agglomerate thereof to obtain Surface-treated magnetic powder 1.

[0533]

<Surface-treated magnetic powder 2>

Surface-treated magnetic powder 2 was prepared similarly as Surface-treated magnetic powder 1 except for using $n\text{-C}_6\text{H}_{13}\text{Si}(\text{OCH}_3)_3$ as silane coupling agent.

[0534]

<Surface-treated magnetic powder 3>

Surface-treated magnetic powder 3 was prepared similarly as Surface treated magnetic powder 1 except for using $n\text{-C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_3)_3$ as the silane coupling agent.

[0535]

<Surface-treated magnetic powder 4>

Surface-treated magnetic powder 4 was prepared similarly as Surface-treated magnetic powder 1 except for using 1.0 wt. part of $n\text{-C}_4\text{H}_9\text{Si}(\text{OCH}_3)_3$ as the silane coupling agent.

[0536]

<Surface-treated magnetic powder 5>

Surface-treated magnetic powder 5 was prepared similarly as Surface treated magnetic powder 1 except for using 0.7 wt. part of $n\text{-C}_4\text{H}_9\text{Si}(\text{OCH}_3)_3$ as the silane coupling agent.

[0537]

<Surface-treated magnetic powder 6>

Surface-treated magnetic powder 6 was prepared similarly as Surface-treated magnetic powder 1 except for using 0.3 wt. part of $n\text{-C}_4\text{H}_9\text{Si}(\text{OCH}_3)_3$ as the silane coupling agent. The above-prepared Surface-treated magnetic powders 1 - 6 are summarized in Table 1 below together with their surface treating agents and amounts thereof.

[0538]

[Table 1]

Surface-treated magnetic powder	Surface-treating agent	Added amount (wt. parts)
1	$n\text{-C}_{10}\text{H}_{21}\text{Si}(\text{OCH}_3)_3$	1.9
2	$n\text{-C}_6\text{H}_{13}\text{Si}(\text{OCH}_3)_3$	1.9
3	$n\text{-C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_3)_3$	1.9
4	$n\text{-C}_4\text{H}_9\text{Si}(\text{OCH}_3)_3$	1.0
5	$n\text{-C}_4\text{H}_9\text{Si}(\text{OCH}_3)_3$	0.7
6	$n\text{-C}_4\text{H}_9\text{Si}(\text{OCH}_3)_3$	0.3

[0539]

<Untreated magnetic powder 1>

Into a ferrous sulfate aqueous solution, a caustic
5 soda solution in an amount of 1.0 - 1.1 equivalent of the ferrous ion was added and mixed to prepare an aqueous solution containing ferrous hydroxide.

[0540]

While maintaining the pH at ca. 9, air was blown
10 into the aqueous solution to cause oxidation at 80 - 90 °C, thereby forming a slurry containing seed crystals.

[0541]

Then, into the slurry, a ferrous sulfate aqueous solution in an amount of 0.9 - 1.2 equivalent of the
15 alkali (i.e., sodium in the caustic soda solution was added, and while maintaining the pH of the slurry at 8, air was blown into the slurry to proceed with oxidation. After the oxidation, the resultant magnetic iron oxide powder was washed, filtered out and dried in
20 an ordinary manner, followed by disintegration of slight agglomerate thereof to obtain Untreated magnetic powder 1.

[0542]

<Electroconductive fine powder 1>

Zinc oxide primary particles having a primary particle size of 0.1 - 0.3 μm were agglomerated under pressure to obtain Electroconductive fine powder 1, which was white in color, and exhibited a volume-
5 average particle size (D_v) of 3.6 μm , a particle size distribution including 6.4 % by volume of particles of 0.5 μm or smaller ($V \% (D \leq 0.5 \mu\text{m}) = 6.4 \% \text{ by volume}$) and 7 % by number of particles of 5 μm or larger ($N \% (D \geq 5 \mu\text{m}) = 7 \% \text{ by number}$), and a resistivity (R_s) of
10 1400 ohm.cm.
[0543]

As a result of observation through a scanning electron microscope (SEM) at magnifications of 3×10^3 and 3×10^4 , Electroconductive fine powder 1 was found to
15 be principally composed of zinc oxide primary particles of 0.1 - 0.3 μm in primary particle size and agglomerated particles of 1 - 5 μm .
[0544]

Electroconductive fine powder 1 also exhibited a
20 transmittance of a mono-particle densest layer with respect to light of 675 nm in wavelength ($T_{675} (\%)$) of ca. 36 % as measured by a transmission densitometer ("310T", available from X-Rite K.K.). The wavelength of 675 nm was identical to the exposure wavelength of a
25 laser beam scanner used in Examples described hereinafter.
[0545]

<Electroconductive fine powder 2>

Electroconductive fine powder 1 was pneumatically classified to obtain Electroconductive fine powder 2, which exhibited $D_v = 2.2 \mu\text{m}$, $V \% (D \leq 0.5 \mu\text{m}) = 4.2 \%$ by volume, $N \% (D \geq 5 \mu\text{m}) = 1 \%$ by number, $R_s = 1400$ ohm.cm and $T_{675} (\%) = 36 \%$.

[0546]

As a result of the SEM observation, Electroconductive fine powder 2 was found to be principally composed of zinc oxide primary particles of $0.1 - 0.3 \mu\text{m}$ in primary particle size and agglomerate particles of $1 - 5 \mu\text{m}$, but the amount of the primary particles was reduced than in Electroconductive fine powder 1.

[0547]

<Electroconductive fine powder 3>

Electroconductive fine powder 1 was pneumatically classified to obtain Electroconductive fine powder 3, which exhibited $D_v = 1.3 \mu\text{m}$, $V \% (D \leq 0.5 \mu\text{m}) = 30 \%$ by volume, $N \% (D \geq 5 \mu\text{m}) = 0 \%$ by number, $R_s = 1400$ ohm.cm and $T_{675} (\%) = 36 \%$.

[0548]

As a result of the SEM observation, Electroconductive fine powder 3 was found to be principally composed of zinc oxide primary particles of $0.1 - 0.3 \mu\text{m}$ in primary particle size and agglomerate particles of $1 - 4 \mu\text{m}$, but the amount of the primary

particles was increased than in Electroconductive powder 1.

[0549]

<Electroconductive fine powder 4>

5 White zinc oxide fine particles were used as Electroconductive fine powder 4, which exhibited $D_v = 0.3 \mu\text{m}$, $V\%$ ($\leq 0.5 \mu\text{m}$) = 81 % by volume, $N\%$ ($\geq 5 \mu\text{m}$) = 0 % by number, primary particle sizes (D_p) = $0.1 - 0.3 \mu\text{m}$, $R_s = 100 \text{ ohm.cm}$, a purity of 99 % or higher and T_{675}
10 (%) = 36 %.

[0550]

As a result of the TEM observation, Electroconductive fine powder 4 was found to be composed of zinc oxide primary particles of $D_p = 0.1 -$
15 $0.3 \mu\text{m}$ and contain little agglomerate particles.

[0551]

<Electroconductive fine powder 5>

Aluminum borate powder surface-coated with antimony tin oxide and having $D_v = 2.5 \mu\text{m}$ was
20 pneumatically classified to remove coarse particles, and then subjected to a repetition of dispersion in aqueous medium and filtration to remove fine particles to recover Electroconductive fine powder 5, which was grayish-white electroconductive fine powder and
25 exhibited $D_v = 3.1 \mu\text{m}$, $V\%$ ($D \leq 0.5 \mu\text{m}$) = 0.7 % by volume, and $N\%$ ($\geq 5 \mu\text{m}$) = 1 % by number.

[0552]

<Developer 1>

Into 709 wt. parts of deionized water, 451 parts of 0.1 M- Na_3PO_4 aqueous solution was added, and after heating to 60 °C, hydrochloric acid was added so as to provide a pH of 6.0 after a subsequent addition of calcium chloride. Thereafter, 67.7 wt. parts of 1.0 M- CaCl_2 aqueous solution was added to form an aqueous medium containing calcium phosphate.

[0553]

10	Styrene	78 wt. part(s)
	n-Butyl acrylate	22 "
	Unsaturated polyester resin	2 "
	(formed by condensation of bisphenol A PO (propylene oxide)- and EO (ethylene oxide)-adduct with fumaric acid)	
15	Saturated polyester resin	3 "
	(formed by condensation of bisphenol A PO- and EO-adduct with terephthalic acid)	
	Negative charge control agent	1 "
20	(monoazo dye-Fe compound)	
	Surface-treated magnetic powder	1 90 "

The above ingredients were uniformly dispersed and mixed by an attritor (made by Mitsui Miike Kakoki K.K.) to form a monomer composition.

25 [0554]

To the monomer composition warmed at 60 °C, 4.5 wt. parts of ester wax (Tabmax (minimum heat-

absorption peak temperature on a DSC curve) = 72 °C) was added to be dissolved therein, and 5 wt. parts of 2,2'-azobis(2,4-dimethylvaleronitrile) (polymerization initiator showing $t_{1/2}$ = 140 min. at 60 °C) was added to
5 be dissolved, thereby forming a polymerizable monomer mixture.

[0555]

The thus-formed polymerizate monomer mixture was charged into the above-prepared aqueous medium and
10 stirred at 60 °C in an N₂ atmosphere for 15 min. at 10,000 rpm by a TK homomixer (made by Tokushu Kika Kogyo K.K.) to disperse the droplets of the monomer mixture. Then, the system was further stirred by a paddle stirrer and subjected to 6 hours of reaction at
15 60 °C. Thereafter, the liquid temperature was raised to 80 °C for further 4 hours of reaction. After the reaction, the system was subjected to 2 hours of distillation at 80 °C. After cooling, hydrochloric acid was added to the suspension liquid to dissolve the
20 calcium phosphate salt. Then, the polymerizate was filtered out, washed with water and dried to recover black-colored particles 1 having a weight-average particle size (D₄) of 7.1 μm.

[0556]

25 Then, 100 wt. parts of black particles 1 were blended with 0.9 wt. part of hydrophobic silica fine powder (S_{BET} = 200 m²/g) which had been successively

treated with hexamethyl-disilazane and silicone oil,
and 1.6 wt. parts of Electroconductive fine powder
shown in Table 2 by means of Henschel mixer to obtain
Developer 1. Some compositional features and

5 properties of Developer 1 are summarized in Table 2.
[0557]

<Developer 2>

Developer 2 was prepared in the same manner as
Developer 1 except for using Surface-treated magnetic
10 powder 2 instead of Surface-treated magnetic powder 1
and using t-butyl peroxy-2-ethylhexanoate as the
polymerization initiator. The properties of Developer
2 are shown in Table 2.

[0558]

15 <Developer 3>

Developer 3 was prepared in the same manner as
Developer 1 except for using Surface-treated magnetic
powder 3 instead of Surface-treated magnetic powder 1
and omitting the pH adjustment by addition of
20 hydrochloric acid to prepare and use an aqueous medium
having a pH of 10.3 for the polymerization. The
properties of Developer 3 are shown in Table 2.

[0559]

<Developer 4>

25 Developer 4 was prepared in the same manner as
Developer 1 except for using Surface-treated magnetic
powder 4 instead of Surface-treated magnetic powder 1.

The properties of Developer 4 are shown in Table 2.

[0560]

<Developer 5>

Developer 5 was prepared in the same manner as
5 Developer 1 except for using Surface-treated magnetic
powder 5 instead of Surface-treated magnetic powder 1.
The properties of Developer 5 are shown in Table 2.

[0561]

<Developer 6>

10 100 wt. parts of Developer particles 1 prepared in
the course of the preparation of Developer 1 were
blended with 0.8 wt. part of hydrophobic silica fine
powder ($S_{BET} = 250 \text{ m}^2/\text{g}$) which had been treated with
hexamethyldisilazane and 1.6 wt. parts of
15 Electroconductive fine powder 3 by a Henschel mixer
(made by Mitsui Miike Kakoki K.K.) shown in Table 2 to
prepare Developer 6. The properties of Developer 6 are
shown in Table 2.

[0562]

20 <Developer 7>

Developer 7 was prepared in the same manner as
Developer 1 except for using 1.5 wt. parts of nigrosin
instead of 1 wt. part of the negative charge control
agent (monoazodye Fe compound) and using 0.9 wt. part
25 of positively chargeable hydrophobic dry-process silica
fine powder ($S_{BET} = 180 \text{ m}^2/\text{g}$) instead of 0.9 wt. part of
the hydrophobic silica fine powder ($S_{BET} = 200 \text{ m}^2/\text{g}$).

The properties of Developer 7 are shown in Table 2.

[0563]

<Developer 8>

Black particles 8 with weight-average particle
5 size of 4.2 μm was prepared by increasing the amount of
 Na_3PO_4 aqueous solution and CaCl_2 aqueous solution in
the manner as Developer 1. Then, 100 wt. parts of
black particles were blended with 1.5 wt. parts of
hydrophobic silica fine powder used in Developer 1 by
10 means of Henschel mixer(made by Mitsui Miike Kakoki
K.K.) to prepare Developer 8. The properties of
Developer 8 are shown in Table 2.

[0564]

<Developer 9>

15 Black particles with weight-average particle size
of 10.4 μm was prepared by increasing the amount of
 Na_3PO_4 aqueous solution and CaCl_2 aqueous solution in
the manner as Developer 1. Then, 100 wt. parts of
black particles were blended with 0.6 wt. parts of
20 hydrophobic silica fine powder used in Developer 1 by
means of Henschel mixer(made by Mitsui Miike Kakoki
K.K.) to prepare Developer 9. The properties of
Developer 9 are shown in Table 2.

[0565]

25 <Developer 10>

Developer 10 was prepared in the same manner as
Developer 1 except for reducing the amount of the ester

wax to 1.2 wt. parts. The properties of Developer 10 are shown in Table 2.

[0566]

<Developer 11>

5 Developer 11 was prepared in the same manner as Developer 1 except for increasing the amount of the ester wax to 54 wt. parts. The properties of Developer 11 are shown in Table 2.

[0567]

10 <Developer 12>

Developer 12 was prepared in the same manner as Developer 1 except for using polyethylene wax (Tabs.max = 100 °C) instead of the ester wax. The properties of Developer 12 are shown in Table 2.

15 [0568]

<Developer 13>

Developer 13 was prepared in the same manner as Developer 1 except for reducing the amount of Surface-treated magnetic powder 1 to 40 wt. parts. The
20 properties of Developer 13 are shown in Table 2.

[0569]

<Developer 14>

Developer 14 was prepared in the same manner as Developer 1 except for increasing the amount of
25 Surface-treated magnetic powder 1 to 150 wt. parts. The properties of Developer 14 are shown in Table 2.

[0570]

<Comparative Developer 1>

Comparative Developer 1 was prepared in the same manner as Developer 1 except for using Surface-treated magnetic powder 6 instead of Surface-treated magnetic powder 1. The properties of Comparative Developer 1 are shown in Table 2.

[0571]

<Comparative Developer 2>

Comparative Magnetic tone 2 was prepared in the same manner as Developer 1 except for using Untreated magnetic powder 1 instead of Surface-treated magnetic powder. The properties of Comparative Developer 2 are shown in Table 2.

[0572]

15 <Developer 15>

Styrene/n-butyl acrylate copolymer 100 wt. part(s)
(weight ratio = 80/20)

	Unsaturated polyester resin	2	"
	Saturated polyester resin	3	"
20	Negative charge control agent (monoazo dye Fe compound)	1	"
	Surface-treated magnetic powder 1	90	"
	Ester wax used in Developer 1	4.5	"

The above ingredients were blended in a blender and melt-kneaded by a twin-screw extruder heated at 105 °C. After being cooled, the kneaded product was coarsely crushed by a hammer mill and finely pulverized

by a jet mill, followed by pneumatic classification to obtain spherical black particles 15 of $D_4 = 8.7 \mu\text{m}$.

Then, 100 wt. parts of black particles 15 were blended with 1.2 wt. parts of the hydrophobic silica fine

5 powder used in Developer 1 and Electro-conductive fine powder shown in Table by a Henschel mixer to obtain Developer 15. The properties of Developer 15 are shown in Table 2.

[0573]

10 <Developer 16>

Black particles 16 of $D_4 = 9.3 \mu\text{m}$ were prepared by changing the pulverization conditions of Developer 15 and after the coarsely crushed product was finely pulverized by a jet mill, followed by pneumatic
15 classification. The classified pulverizate was surface-treated by an impact-type surface treatment apparatus under the conditions of treatment temperature of 50°C and a rotor blade peripheral speed of 90 m/sec. Then, 100 wt. parts of black particles 16 were
20 blended with 1.2 wt. parts of the hydrophobic silica used in Developer 6 per 100 wt. parts of the black parties and Electroconductive fine powder shown in Table 2 by a Henschel mixer to obtain Developer 16 The properties of Developer 16 are shown in Table 2.

25 [0574]

<Developer 17>

Black particles 17 of $D_4 = 8.6 \mu\text{m}$ were prepared

similarly as Developer 15 except for pulverizing the coarsely crushed product by means of a turbo mill (Made by Turbo Kogyo K.K.), followed by treatment by an impact-type surface treating apparatus (treatment temperature = 50 °C, rotating blade peripheral speed = 90 m/sec).

[0575]

Then, 100 wt. parts of black particles 17 were blended with 1.0 wt. parts of the hydrophobic colloidal silica used in Developer 6 per 100 wt. parts of the black particles and Electroconductive fine powder shown in Table 2 by a Henschel mixer to obtain Developer 17. The properties of Developer 17 are shown in Table 2.

[0576]

15 <Developers 18 - 20>

Developers 18 - 20 were prepared by blending the black particles 1 obtained in Developer 1 with 0.9 wt. parts of the hydrophobic colloidal silica used in Developer 1 and Electroconductive fine powder using a Henschel mixer to obtain Developers 18 - 20, respectively. The properties of Developers 18 - 20 are shown in Table 2.

[0577]

As for magnetization measured at a magnetic field of 79.6 kA/m, Developer 13 exhibited 17.3 Am²/kg, Developer 14 exhibited 37.2 Am²/kg, and all the other Developers exhibited values in the range of 26 - 30

$\text{Am}^2/\text{kg}.$

[0578]

[Table 2]

Developer	Magnetic powder		Wax wt. parts	Charge control agent	D4 (μ m)	Circularity		Isolated iron particles (%)	External additive		
	Magnetic powder used	wt. parts				C av	C mode		Silica	Conductive powder	wt. parts
									species	wt. part(s)	name
1	Surface treated 1	90	Ester 4.5	monoazo Fe	7.1	0.983	1.00	0.21	*1	0.9	3
2	Surface treated 2	↑	↑	↑	6.8	0.984	1.00	0.29	↑	↑	↑
3	Surface treated 3	↑	↑	↑	7.0	0.987	1.00	0.10	↑	↑	↑
4	Surface treated 4	↑	↑	↑	6.7	0.982	1.00	1.71	↑	↑	↑
5	Surface treated 5	↑	↑	↑	6.6	0.983	1.00	2.80	↑	↑	↑
6	Surface treated 1	↑	↑	↑	7.1	0.984	1.00	0.21	*2	0.8	3
7	↑	↑	↑	nigrosin	7.0	0.982	1.00	0.14	*3	0.9	3
8	↑	↑	↑	monoazo Fe	4.2	0.986	1.00	0.18	*1	1.5	4
9	↑	↑	↑	↑	10.4	0.972	1.00	0.24	*1	0.6	3
10	↑	↑	Ester 1.2	↑	6.1	0.990	1.00	0.14	*1	0.9	3
11	↑	↑	Ester 54	↑	8.3	0.975	1.00	0.99	↑	↑	↑
12	↑	↑	poly- ethylene 4.5	↑	7.7	0.974	1.00	0.95	↑	↑	↑
13	↑	40	Ester 4.5	↑	7.9	0.990	1.00	0.07	↑	↑	↑
14	↑	150	↑	↑	6.1	0.976	1.00	1.92	↑	↑	↑
15	↑	90	↑	↑	8.7	0.928	0.95	1.45	*1	1.2	3
16	↑	↑	↑	↑	9.3	0.952	0.96	1.61	*1	1.2	3
17	↑	↑	↑	↑	8.6	0.963	0.97	1.51	*2	1.0	3
18	↑	↑	↑	↑	7.1	0.983	1.00	0.21	*1	0.9	2
19	↑	↑	↑	↑	7.1	0.983	1.00	0.21	*1	0.9	1
20	↑	↑	↑	↑	7.1	0.983	1.00	0.21	*1	0.9	5
Comp. 1	Surface treated 6	↑	↑	↑	7.2	0.982	1.00	3.28	*1	1.2	3
Comp. 2	Untreated 1	↑	↑	↑	5.6	0.970	1.00	3.52	↑	↑	↑

*1: silica treated with hexamethyl disilazane and silicon oil

*2: silica treated with hexamethyl disilazane

*3: positively chargeable hydrophobic dry-process silica

[0579]

<Image-bearing member 1>

An electroconductive substrate of Al cylinder having an outer diameter of 3 mm, a thickness of 3 mm
5 was successively coated with a charge injection-barrier layer, a photoconductor layer, a buffer layer and a surface layer by using a plasma CVD apparatus shown in Fig. 7 respectively under the following conditions to
10 surface layer.

[0580]

(Conditions to prepare photoreception member)

Change injection-barrier layer:

	SiH ₄	300 ml/min (under NTP = 298 K/105 Pa)
15	H ₂	500 ml/min (NTP)
	NO	8 ml/min (NTP)
	PH ₃	800 ppm (based on SiH ₄)
	Power	400 W (13.56 MHz)
	Internal press.	53.3 Pa
20	Substrate temp.	250 °C
	Thickness	1 μm

Photoconductor layer:

	SiH ₄	500 ml/min (NTP)
	H ₂	500 ml/min (NTP)
25	Power	800 W (13.56 MHz)
	Internal press.	66.7 Pa
	Substrate temp.	250 °C

Thickness 20 μm

Buffer layer:

SiH_4 50 ml/min

CH_4 350 ml/min (NTP)

5 Power 200 W (13.56 MHz)

Internal press. 66.7 Pa

Substrate temp. 250 $^{\circ}\text{C}$

Thickness 0.2 μm

[0581]

10 (Conditions to prepare surface layer of Image-bearing member 1)

SiH_4 20 ml/min

CH_4 500 ml/min (NTP)

Power 300 W (13.56 MHz)

15 Internal press. 40.0 Pa

Substrate temp. 250 $^{\circ}\text{C}$

[0582]

<Image-bearing member 2>

An electroconductive substrate of Al cylinder
20 having an outer diameter of 3 mm, a thickness of 3 mm
was successively coated with a charge injection-barrier
layer, a photoconductor layer, a buffer layer and a
surface layer by using a plasma CVD apparatus shown in
Fig. 8 respectively under the following conditions to
25 prepare Image-bearing member 2 having a 0.2 μm -thick
surface layer.

[0583]

(Conditions to prepare photoreception member)

Charge injection-barrier layer:

	SiH ₄	100 ml/min (under NTP)
	H ₂	500 ml/min (NTP)
5	NO	5 ml/min (NTP)
	PH ₃	500 ppm (based on SiH ₄)
	Power	100 W (105 MHz)
	Internal press.	1.0 Pa
	Substrate temp.	250 °C
10	Thickness	1 μm

Photoconductor layer:

	SiH ₄	500 ml/min (NTP)
	H ₂	500 ml/min (NTP)
	Power	300 W (105 MHz)
15	Internal press.	1.0 Pa
	Substrate temp.	250 °C
	Thickness	15 μm

Buffer layer:

	SiH ₄	50 ml/min
20	CH ₄	500 ml/min (NTP)
	Power	300 W (105 MHz)
	Internal press.	1.0 Pa
	Substrate temp.	250 °C
	Thickness	0.2 μm

25 [0584]

(Conditions to prepare surface layer of Image-bearing member 2)

CH₄ 500 ml/min (NTP)
Power 1000 W (105 MHz)
Internal press. 0.27 Pa
Substrate temp. 100 °C

5 [0585]

<Image-bearing member 3>

An electroconductive substrate of Al cylinder having an outer diameter of 3 mm, a thickness of 3 mm was successively coated with a charge injection-barrier layer, a photoconductor layer, a buffer layer and a surface layer by using a plasma CVD apparatus shown in Fig. 7 respectively under the following conditions to prepare Image-bearing member 3 having a 0.5 µm-thick surface layer.

15 [0586]

(Conditions to prepare photoreception member)

SiH₄ 100 ml/min (under NTP)
H₂ 300 ml/min (NTP)
NO 5 ml/min (NTP)
20 B₂H₆ 2000 ppm (based on SiH₄)
Power 400 W (13.56 MHz)
Internal press. 53.3 Pa
Substrate temp. 290 °C
Thickness 2 µm

25 Photoconductor layer:

SiH₄ 200 ml/min (NTP)
H₂ 800 ml/min (NTP)

B₂H₆ 1 ppm (based on SiH₄)

Power 800 W (13.56 MHz)

Internal press. 66.7 Pa

Substrate temp. 290 °C

5 Thickness 27 μm

[0587]

(Conditions to prepare surface layer of Image-bearing member 3)

Surface layer:

10 SiH₄ 10 ml/min (NTP)

CH₄ 500 ml/min (NTP)

Power 300 W (13.56 MHz)

Internal press. 66.7 Pa

Substrate temp. 290 °C

15 [0588]

<Comparative Image-bearing member 1>

Photosensitive member having a laminar structure as shown in Fig. 10 was prepared by successively forming the following layers by dipping on a 30 mm-dia.

20 Aluminum cylinder.

[0589]

(1) Electroconductive coating layer: a 15 μm-thick layer, principally comprising phenolic resin with powder of tin oxide and titanium oxide dispersed
25 therein.

(2) Undercoating layer: a 0.6 μm-thick layer comprising principally modified nylon and copolymer

nylon.

(3) Charge generation layer: a 0.6 μm -thick layer comprising principally an azo pigment having an absorption peak in a long-wavelength region dispersed
5 within butyral resin.

(4) Charge transport layer: a 25 μm -thick layer comprising principally a hole-transporting triphenylamine compound dissolved in polycarbonate resin (having a molecular weight of 2×10^4 according to
10 the Ostwald viscosity method) in a weight ratio of 8:10 and further containing 10 wt. % based on total solid of polytetrafluoroethylene powder (volume-average particle size (D_v) = 0.2 μm) dispersed therein.

The layer surface exhibited a contact angle with
15 pure water of 95 deg. as measured by a contact angle meter ("CA-X, available from Kyowa Kaimen Kagaku K.K.) to provide Comparative Image-bearing member 1.

[0590]

<Charging member 1>

20 Charging roller was prepared in the following manner. A SUS (stainless steel)-made roller of 9 mm in diameter and 346 mm in length was used as a core metal and coated with a medium resistivity roller-form foam urethane layer formed from a composition of urethane
25 resin, a vulcanizing agent and a foaming agent, followed by cutting and polishing for shape and surface adjustment to obtain a charging roller having a

flexible foam urethane coating layer of 16 mm in outer diameter and 318 mm in length.

[0591]

The thus-obtained charging roller exhibited a
5 resistivity of 10^5 ohm.cm and an Asker C hardness of 30 deg. with respect to the foam urethane layer. As a result of observation through a scanning electron microscope, the charging roller surface was covered with concave cells showing an average cell diameter of
10 ca. 100 μ m and a cell areal percentage of 65 % to provide Charging member 1.

[0592]

<Charging member 2>

About a SUS roller of 9 mm in diameter and 346 mm
15 in length as a core metal, a tape of piled electroconductive nylon fiber was spirally wound to prepare a charging brush roller. The electroconductive nylon fiber was formed from nylon in which carbon black was dispersed for resistivity adjustment and comprised
20 yarns of 6 denier (composed of 50 filament of 300 denier). The nylon yarns in a length of 3 mm were planted at a density of 10^5 yarns/in² to provide a brush roller exhibiting a resistivity of 1×10^7 ohm.cm to provide Charging member 2.

25 [0593]

<Charging member 3>

To a mixture of Fe₂O₃ 50 mol. %, CuO 25 mol. % and

ZnO 25 mol. %, 0.05 wt. % of phosphorus was added together with a dispersing agent, a binder agent and water, and the mixture was subjected to dispersion and mixing in a ball mill and then formed into particles by
5 a spray dryer. Then, the particles were calcined at 1150 °C for 6 hours, and the calcined particles were then disintegrated and classified by a dispersion separator to obtain spherical ferrite particles of Dv. 50% = 35 µm.

10 [0594]

100 wt. parts of the ferrite particles were blended with a solution of 0.10 wt. parts of a titanium coupling agent (isopropoxy-triisostearoyl titanate) in toluene to be wet-coated with the latter, and then
15 cured at 170 °C in an electric oven to prepare magnetic particles forming a magnetic brush. The magnetic particles exhibited a volume resistivity of 3.5×10^7 ohm.cm.

[0595]

20 Separately, for having the magnetic particles form a magnetic brush, a magnet roller giving a magnetic flux density of 0.1 T (tesla) was enclosed within an aluminum cylinder having an outer diameter of 16 mm to form an electrode sleeve, which was designed to be
25 disposed with a gap of ca. 500 µm from a photosensitive member and then coated with the above prepared magnetic particles at a rate of 170 mg/m² to provide Charging

member 3.

[0596]

<Example 1>

An image forming apparatus having an organization
5 as illustrated in Fig. 2 was provided by remodeling a
commercially available copying machine using laser light
for digital latent image formation ("GP-405" made by
Canon K.K.).

[0597]

10 Image-bearing member 1 prepared in the above-
described manner was used as an image-bearing member 1.
Against the image-bearing member 1, Charging member 1
as a primary charging member was abutted at a
prescribed pressure in resistance to its elasticity and
15 a DC charging bias voltage of -440 volts was applied to
the core metal of the charging member while rotating
the charging member while rotating the charging member
306 at a peripheral speed of -100 % relative to that of
the image-bearing member 1 in a counter direction with
20 respect to the image-bearing member 1, i.e., at a
relative speed ratio of 100 %, thereby uniformly
charging the image-bearing member 1. The charging
member surface was uniformly coated with
Electroconductive fine powder 3 at rate of 1×10^4
25 particles/mm² while operating an electroconductive fine
powder-supply mechanism. The thus primary charged
image-bearing member 1 surface was exposed to imagewise

laser light having a wavelength of 675 nm to form an electrostatic latent image comprising a dark-part potential (Vd) of -400 volts and light-part potential (Vl) of -20 volts respectively as an average of
5 potentials measured at three points on the image-bearing member when brought to a position closest to the developing sleeve.

[0598]

The developing sleeve was disposed with a gap of
10 200 μm from the image-bearing member (photosensitive drum), and comprised a 20 mm-dia. Aluminum cylinder surface-blasted with glass beads and then coated with a ca. 10 μm -thick resin layer formed from the following composition so as to have a JIS center line-average
15 roughness (Ra) of 0.85 μm .

Phenolic resin	100 wt. parts
Graphite	36 "
(particle size = ca. 7 μm)	
Carbon black	4 "

20 Inside the developing sleeve 12, a fixed multi-pole magnet 14 including a developing pole S1 of 95 mT (950 Gauss), and a knife edge-shaped ferromagnetic blade 11a (of Fe-Ni alloy) having a tapered portion toward the photosensitive member 1 was disposed with a
25 gap of 210 μm from the sleeve.

[0599]

For the development, a developing bias voltage of a

DC component of $V_{dc} = -270$ volts and an AC component of $V_{pp} = 800$ volts and $f = 1900$ Hz in superposition. The developing sleeve 12 was rotated to provide a peripheral speed of 378 mm/sec which was 180 % of a
5 peripheral speed 8210 mm/sec) of the image-bearing member 1 in an identical direction. A transfer device 302 for the commercial apparatus was replaced by one of a corona transfer-type.

[0600]

10 Further, a pre-exposure device emitting light having a wavelength of 660 nm was disposed between the cleaning member and the charging member. A hot roller fixing device 313 included in GP405 was used as it was.

[0601]

15 In this Example, Developer 1 was used for continuous image formation on plain paper of 64 g/m^2 as a transfer material P in a normal temperature/normal humidity environment while replenishing Developer 1 as required. As a result, good images free from transfer
20 dropout of character and line images, back soil due to offset or fog at non-image parts, were obtained at the initial stage.

[0602]

Then, for evaluating image forming performances in
25 more details, an A4-lateral size image of a test chart ("TC-A1 Chart: FY9-9045-000", made by Canon K.K.) was reproduced on 20,000 sheets in a continuous mode in

various environments described hereinafter, and image evaluation was performed with respect to the following items.

[0603]

5 (1) Image density (I.D.)

An image density formed on plain paper for copying (64 g/m²) was measured relative to the density (0.00) at the non-image portion by using a Macbeth reflection densitometer ("RD 918", made by Macbeth Co.). Based on
10 the measured image density, the evaluation was performed according to the following standard:

- A: ≥ 1.40 (very good)
- B: ≥ 1.35 and < 1.40 (good)
- C: ≥ 1.00 and < 1.35 (practically of no problem)
- 15 D: < 1.00 (somewhat problematic)

[0604]

(2) Fog

Fog density (%) was measured as a difference in whiteness (reflectance) between a white background
20 portion of printed image and a blank white paper as measured by a reflectometer ("MODEL TC-6DS", made by Tokyo Denshoku K.K.). Based on the measured fog density, the evaluation was performed according to the following standard.

- 25 A: < 1.0 % (very good)
- B: ≥ 1.0 % and < 2.0 % (good)
- C: ≥ 2.0 % and < 3.0 % (practically of no

problem)

D: > 3.0 % (somewhat problematic)

[0605]

(3) Transferability (transfer efficiency)

5 Transfer residual toner remaining on the
photosensitive member after formation and transfer of a
solid black image (by using a test chart "FY9-9073-
000", made by Canon K.K.) was peeled off with a
polyester adhesive tape, and the adhesive tape was
10 applied on a white paper to measure a Macbeth density
(denoted by "C"). An identical polyester adhesive tape
was applied on the solid black image transferred onto
white paper to measure a Macbeth density (denoted by
"D"). An identical polyester adhesive tape was applied
15 on a blank white paper to measure a Macbeth density
(denoted by "E"). Based on the measured density
values, a transfer efficiency is calculated according
to the formula:

[Mathematical Formula 7]

20 Transfer efficiency (%) = $\{(D-C)/(D-E)\} \times 100$. An
image has no problem when the measured transfer
efficiency value is 90 % or higher.

[0606]

(4) Resolution

25 Resolution was measured in accordance with the
following procedure. Namely, an original image with
the pattern consisting of five thin lines with equal

line width and interval that the lines were drawn as if there are 2.8, 3.2, 3.6, 4.0, 4.5, 5.0, 5.6, 6.3, 7.1 or 8.0 lines in 1 mm was prepared. The original sheets having these ten types of line image were copied under
5 the appropriate copying conditions. Then the copied images were examined using a magnifier and number of lines of images where the lines were clearly separated (line/mm) was counted to obtain the resolution values. The larger value means higher resolution.

10 [0607]

(5) Image roughening

An image forming apparatus including a photosensitive member and a toner to be tested was left to stand for at least 72 hours in each test
15 environment. Thereafter, continuous copying was performed on 20,000 sheets, and then power supply to the apparatus was turned off, followed by standing for 24 hours in the environment. Thereafter, the below charts used for continuous reproduction on 100 sheets.

20 [0608]

For copied sheets for evaluating the images, halftone charts ("FY9-9042-000" and "FY9-9098-000", both made by Canon K.K.) were used.

[0609]

25 Image unevenness of the reproduced halftone images were evaluated visually.

[0610]

The evaluation standard is as shown below.

A: Halftone density irregularity could not be recognizable with eyes.

B: Recognition of halftone image irregularity
5 was almost impossible with eyes.

C: Halftone density irregularity could be recognizable with eyes.

D: Halftone density irregularity was clearly recognizable with eyes.

10 [0611]

Test environments (temperature and humidity) were selected as follows:

HT/HH: 30 ± 2 °C/ 80 ± 10 % RH

HT/HH: 25 ± 2 °C/ 50 ± 10 % RH

15 HT/HH: 25 ± 2 °C/ 10 ± 5 % RH

HT/HH: 15 ± 2 °C/ 10 ± 5 % RH

When image quality was differed due to environment, the evaluation was made using an image having the worst quality.

20 [0612]

The above items (1) - (4) were evaluated in the normal temperature/normal humidity (NT/NH) environment, and the item (5) was evaluated in all the environment. Each test image formation was performed while turning
25 off the drum heater as an anti-humidity measure. Further, the continuous image formation was basically performed by using the "TC-A1 Chart: FY9-9045-000",

made by Canon K.K.), and specific test charts for respective items were used at an appropriate point of and after the continuous image formation.

For evaluation items (1) - (5), the evaluation
5 results of images both at the initial stage and after 20,000 sheets of copying are inclusively shown in Tables 3 and 4.

[0613]

Incidentally, in the following Examples an
10 identical species of Electroconductive fine powder as contained in Developer to be tested was supplied by application to the charging member.

<Example 2>

Image formation and evaluation were performed in
15 the same manner as Example 1 except for using Image-bearing member 2 instead of Image-bearing member 1 and Developer 2 instead of Developer 1. The obtained evaluation results are shown in Tables 3 and 4.

[0614]

20 <Example 3>

Image formation and evaluation were performed in the same manner as in Example 1 except for omitting the replacement of the transfer device to a corona transfer device and using Developer 3 instead of Developer 1.
25 The obtained evaluation results are shown in Tables 3 and 4.

[0615]

<Examples 4 - 6>

Image formation and evaluation were performed in the same manner as in Example 1 except for using Developers shown in Tables 3 and 4 in each Example instead of Developer 1. The obtained evaluation results are shown in Tables 3 and 4.

[0616]

<Example 7>

Image formation and evaluation were performed in the same manner as in Example 1 except for using Developer 7 (positively chargeable toner) instead of Developer 1, and using Image-bearing member 3 (positively chargeable) instead of Image-bearing member 1, and changing the polarities of the charging bias voltage, and DC-component of the developing bias voltage and the transfer bias voltage to opposite to those applied in Example 1. The obtained evaluation results are shown in Tables 3 and 4.

[0617]

20 <Examples 8 - 20>

Image formation and evaluation were performed in the same manner as in Example 1 except for using Developers shown in Tables 3 and 4 in each Example instead of Developer 1. The obtained evaluation results are shown in Tables 3 and 4.

[0618]

<Example 21>

Image formation and evaluation were performed in the same manner as in Example 1 except for charging the image-bearing member to $V_d = -590$ volts and $V_1 = -140$ volts and changing the DC component (V_{dc}) of the
5 developing bias voltage to -440 volts. The obtained evaluation results are shown in Tables 3 and 4.

[0619]

<Example 22>

Image formation and evaluation were performed in
10 the same manner as in Example 1 except for charging the image-bearing member to $V_d = -540$ volts and $V_1 = -100$ volts and changing V_{dc} of the developing bias voltage to -400 volts. The obtained evaluation results are shown in Tables 3 and 4.

15 [0620]

<Example 23>

Image formation and evaluation were performed in the same manner as in Example 1 except for charging the image-bearing member to $V_d = -490$ volts and $V_1 = -80$
20 volts and changing V_{dc} to -360 volts. The obtained evaluation results are shown in Tables 3 and 4.

[0621]

<Example 24>

Image formation and evaluation were performed in
25 the same manner as in Example 1 except for charging the image-bearing member to $V_d = -310$ volts and $V_1 = -10$ volts and changing V_{dc} to -200 volts. The obtained

evaluation results are shown in Tables 3 and 4.

[0622]

<Example 25>

Image formation and evaluation were performed in
5 the same manner as in Example 1 except for charging the
image-bearing member to $V_d = -290$ volts and $V_1 = -5$
volts and changing V_{dc} to -190 volts. The obtained
evaluation results are shown in Tables 3 and 4.

[0623]

10 <Example 26>

Image formation and evaluation were performed in
the same manner as in Example 1 except for changing the
peripheral speed of the image-bearing member to 263
mm/sec while retaining the charging roller peripheral
15 speed and changing the developing sleeve to $R_a = 1.10$
 μm and the peripheral speed to 426 mm/sec. The
obtained evaluation results are shown in Tables 3 and
4.

[0624]

20 <Example 27>

Image formation and evaluation were performed in
the same manner as in Example 1 except for using
Charging member 2 instead of Charging member 1, while
omitting the electroconductive fine powder-application
25 mechanism, modifying so as to drive at the relative
speed difference of 100% of the relative moving speed
ratio in the opposite direction at the contact point to

the surface of the image-bearing member, and applying a charging bias voltage of -450 volts to the core metal of the charging member. The obtained evaluation results are shown in Tables 3 and 4.

5 [0625]

<Example 28>

Image formation and evaluation were performed in the same manner as in Example 1 except for using Charging member 3 instead of Charging member 1 while
10 omitting the electroconductive fine powder-application mechanism and operating Charging member 3 so that its electrode sleeve peripheral moving direction was opposite to that of the image bearing member so as to provide a relative speed ratio of 150 % while fixing
15 the magnet roll therein to form a magnetic brush rubbing the image-bearing member surface. Then, the electrode sleeve was supplied with a charging voltage of $V_{dc} = -450$ volts and $V_{ac} = 0.5$ k-volts (peak-to-peak) in superposition to charge the image-bearing
20 member. The obtained evaluation results are shown in Tables 3 and 4.

[0626]

<Comparative Example 1>

Image formation and evaluation were performed in
25 the same manner as in Example 1 except for using Comparative Developer 1 instead of Developer 1. The obtained evaluation results are shown in Tables 3 and

4.

[0627]

<Comparative Example 2>

Image formation and evaluation were performed in
5 the same manner as in Example 1 except for using
Comparative Developer 2 instead of Developer 1. The
obtained evaluation results are shown in Tables 3 and
4.

[0629]

10 <Comparative Example 3>

Image formation and evaluation were performed in
the same manner as in Example 1 except for using
Comparative Image-bearing member 1 instead of Image-
bearing member 1 and changing the relative speed ratio
15 to 150 % so as to provide identical dark potential to
the image-bearing member, while retaining the moving
direction of the charging member. The obtained
evaluation results are shown in Tables 3 and 4.

[0629]

20 <Comparative Example 4>

The contact charging member of GP 405" was used as
it was as charge photosensitive member 1 by applying a
charging bias voltage as in Example 1, but the charging
potential of the image-bearing member could not reach
25 to the desired level.

[0630]

<Comparative Example 5>

Image formation and evaluation were performed in the same manner as in Example 1 except for charging the image-bearing member to $V_d = -650$ volts and $V_1 = -150$ volts and changing V_{dc} (of the developing bias voltage) to -480 volts. The obtained evaluation results are shown in Tables 3 and 4.

<Comparative example 6>

Image formation and evaluation were performed in the same manner as in Example 1 except for charging the image-bearing member to $V_d = -240$ volts and $V_1 = 0$ volt and changing V_{dc} to -170 volts. The obtained evaluation results are shown in Tables 3 and 4.

[0631]

[Table 3]

Example	NT/NH (Initial)				NT/NH (after 20,000 sheets)			
	I.D.	Fog	Transfer- ability (%)	Resolution	I.D.	Fog	Transfer- ability (%)	Resolution
1	A	A	97	8.0	A	A	96	7.1
2	A	A	97	7.1	A	A	95	7.1
3	A	A	98	7.1	A	A	97	7.1
4	A	A	94	6.3	B	B	94	5.6
5	B	B	92	6.3	C	C	91	5.6
6	A	A	95	7.1	A	A	92	5.6
7	A	A	96	7.1	A	A	94	6.3
8	B	B	92	8.0	B	C	91	7.1
9	A	A	95	6.3	A	A	92	5.6
10	A	A	96	7.1	A	A	94	6.3
11	B	B	92	5.6	C	C	90	5.6
12	A	A	96	7.1	A	A	94	6.3
13	B	B	94	6.3	B	C	92	5.6
14	A	B	93	6.3	A	B	91	6.3
15	B	B	91	5.0	B	C	90	4.5
16	A	B	92	5.6	A	C	90	5.0
17	A	B	93	6.3	A	C	91	5.6
18	A	A	97	8.0	A	A	96	7.1
19	A	A	97	8.0	A	A	96	7.1
20	A	A	97	8.0	A	A	95	7.1
21	A	B	97	7.1	A	B	94	6.3
22	A	A	97	6.3	A	A	95	5.6
23	A	A	97	7.1	A	A	95	6.3
24	A	B	97	7.1	B	B	95	6.3
25	B	B	96	6.3	B	C	95	5.6
26	A	A	95	7.1	A	A	93	6.3
27	A	A	97	7.1	A	A	95	6.3
28	A	A	97	7.1	A	A	95	6.3
Comp. 1	A	C	92	5.6	B	C	88	5.0
Comp. 2	B	C	89	5.0	B	D	80	4.0
Comp. 3	A	B	93	6.0	-	-	-	-
Comp. 5	A	A	96	7.1	-	-	-	-
Comp. 6	D	B	96	7.1	D	C	94	6.3

[0632]

[Table 4]

thereafter.

[0634]

In all Examples except for Examples 10 and 12, good images free from ghost and back soiling of the copied images were obtained without causing soiling of the image-bearing member, the transfer device and the fixing device. In Examples 10 and 12, slight toner soiling was observed on the pressure roller in the fixing device after the continuous image formation test but no images were accompanied with back surface soiling.

[0635]

In the above-mentioned image forming methods (apparatuses) in Examples, no ozone smell was recognized.

[0636]

<Example 29>

An image forming apparatus (so-called cleanerless apparatus) having an organization obtained by removing the cleaning device and the electroconductive fine powder-application mechanism from the apparatus used in Example 1, was used on 50,000 sheets, and evaluated with respect to identical items as in Example 1. Before each continuous image formation, Electroconductive fine powder 3 was applied onto the surface of Charging member 1 at a coating rate of ca. 1×10^4 particles/mm². For evaluating the matching

between the image-bearing member and the charging method, and potential difference (lowering) V_d (volts) between the initial stage and after 50,000 sheets of the continuous image formation was measured.

5 [0637]

After the copying on 50,000 sheets, an adhesive tape was applied onto a surface on the charging roller to recover the attached powder which was found to uniformly cover the roller and recognized to almost
10 comprise white zinc oxide particles (Electroconductive fine powder 1) while a slight amount of transfer residual toner was recognized. The electroconductive fine powder was measured to be present at a density of ca. 2×10^5 particles/mm². As a result of observation
15 through a scanning electron microscope, the transfer residual toner particles were free from electroconductive fine powder sticking thereonto. The results of performance evaluation in this Example are summarized in Table 4 together with those of the
20 following Examples.

[0638]

In each of the following Examples, Electroconductive fine powder contained in each Developer used was applied onto the charging member in
25 advance of the continuous image formation.

<Example 30 - 34>

Image formation and evaluation were performed in

the same manner as in Example 29 except for using Developers shown in Table 5 in each Example instead of Developer 1. The obtained evaluation results are shown in Table 5.

5 [0639]

<Example 35>

Image formation and evaluation were performed in the same manner as in Example 7 except for using an image forming apparatus formed by removing the cleaner
10 and the electroconductive fine powder application mechanism. The obtained evaluation results are shown in Table 5.

[0640]

<Examples 36 - 48>

15 Image formation and evaluation were performed in the same manner as in Example 29 except for using Developers shown in Table 5 in each Example instead of Developer 1. The obtained evaluation results are shown in Table 5.

20 [0640]

<Examples 36 - 55>

Image formation and evaluation were performed in the same manner as in Example 29 except for using Developers shown in Table 5 in each Example nstead of
25 Developer 1. The obtained evaluation results are shown in Table 5.

[0640]

Example	Halftone image roughness				Developer used
	HT/HH	NT/NH	NT/LH	LT/LH	
1	A	A	A	A	Developer 1
2	A	A	A	A	Developer 2
3	A	A	A	A	Developer 3
4	B	A	B	B	Developer 4
5	B	B	C	C	Developer 5
6	A	A	B	B	Developer 6
7	A	A	A	A	Developer 7
8	C	B	C	B	Developer 8
9	B	B	C	B	Developer 9
10	A	A	A	A	Developer 10
11	A	B	B	B	Developer 11
12	B	B	C	B	Developer 12
13	B	B	C	C	Developer 13
14	C	B	C	B	Developer 14
15	C	B	C	C	Developer 15
16	B	B	B	B	Developer 16
17	B	B	B	B	Developer 17
18	A	A	A	A	Developer 18
19	A	A	A	A	Developer 19
20	A	A	A	A	Developer 20
21	A	A	B	B	Developer 1
22	A	A	B	A	Developer 1
23	A	A	A	A	Developer 1
24	A	A	A	A	Developer 1
25	A	B	B	A	Developer 1
26	A	A	A	A	Developer 1
27	A	A	A	A	Developer 1
28	A	A	A	A	Developer 1
Comp. 1	B	C	C	C	Comp. Developer 1
Comp. 2	C	C	D	D	Comp. Developer 2
Comp. 3	-	-	-	-	Developer 1
Comp. 5	-	-	-	-	Developer 1
Comp. 6	B	C	C	C	Developer 1

[0633]

In Comparative Example 3, image defects attributable to charging irregularity occurred after continuous copying on 15,000 sheets, so that the image formation and evaluation were terminated. In comparative Example 5, charge leakage occurred on the image-bearing member after 1000 sheets, so that the image formation and evaluation were terminated

Image formation and evaluation were performed in the same manner as in Example 29 except for operating the image forming apparatus of Example 29 under the conditions specified in Table 5, respectively. The
5 obtained evaluation results are shown in Table 5.

[0641]

<Comparative Examples 7 - 8>

Image formation and evaluation were performed in the same manner as in Example 29 except for using
10 Developers shown in Table 5 in each Example instead of Developer 1. The obtained evaluation results are shown in Table 5. In comparative Example 8, charging failure occurred after copying on 1000 sheets, so that the evaluation could not be made.

15 [0642]

[Table 5]

Example	Developer used	NT/NH (Initial)				NT/NH (After 50000 sheets)				Halftone image roughening				v (-volts)	Electro-conductive fine powder
		I.D.	Fog	Transfer-ability (%)	Resolu-tion	I.D.	Fog	Transfer-ability (%)	Resolu-tion	HT/ HN	NT/ NH	NT/ LH	LT/ LH		
29	1	A	A	97	8.0	A	A	96	7.1	A	A	A	A	5	2 x 10 ⁵
30	2	A	A	97	7.1	A	A	95	7.1	A	A	A	A	5	3 x 10 ⁵
31	3	A	A	98	7.1	A	A	97	7.1	A	A	A	A	5	2 x 10 ⁵
32	4	A	A	94	6.3	B	B	94	5.6	B	A	B	B	5	2 x 10 ⁵
33	5	B	B	92	5.6	C	C	91	5.0	B	B	C	C	15	2 x 10 ⁵
34	6	A	A	95	7.1	A	B	92	5.0	A	A	B	B	15	7 x 10 ⁵
35	7	A	A	96	7.1	A	A	94	6.3	A	A	A	A	10	5 x 10 ⁵
36	8	B	B	92	6.3	B	C	91	5.6	C	B	C	C	15	1 x 10 ⁵
37	9	A	A	95	6.3	A	A	92	5.6	B	B	C	B	5	6 x 10 ⁵
38	10	A	A	96	7.1	A	A	94	6.3	A	A	A	A	5	2 x 10 ⁵
39	11	B	B	92	5.6	C	C	90	5.0	A	B	B	C	15	9 x 10 ⁵
40	12	A	A	96	7.1	A	A	94	6.3	B	B	C	B	5	8 x 10 ⁵
41	13	B	B	94	5.6	B	C	92	5.0	B	B	C	C	10	7 x 10 ⁵
42	14	A	B	93	6.3	A	B	91	5.6	C	B	C	C	10	9 x 10 ⁵
43	15	B	B	91	5.0	B	C	90	4.5	C	B	C	C	15	2 x 10 ⁵
44	16	A	B	92	5.6	A	C	90	5.0	B	B	C	C	15	6 x 10 ⁵
45	17	A	B	93	6.3	A	C	91	5.0	B	B	C	B	10	4 x 10 ⁵
46	18	A	A	97	8.0	A	A	96	7.1	A	A	A	A	0	8 x 10 ⁵
47	19	A	A	97	8.0	A	A	96	7.1	A	A	A	A	5	5 x 10 ⁵
48	20	A	A	97	8.0	A	A	95	7.1	A	A	A	A	5	7 x 10 ⁵
49	1	A	B	97	7.1	A	B	94	6.3	A	A	B	B	5	9 x 10 ⁵
50	1	A	A	97	6.3	A	A	95	5.6	A	A	B	A	5	6 x 10 ⁵
51	1	A	A	97	7.1	A	A	95	6.3	A	A	A	A	5	4 x 10 ⁵
52	1	A	B	97	7.1	B	B	95	6.3	A	A	A	A	5	9 x 10 ⁵
53	1	B	B	96	6.3	B	C	95	5.6	A	B	B	A	5	6 x 10 ⁵
54	1	A	A	95	7.1	A	A	93	6.3	A	A	A	A	5	3 x 10 ⁵
55	1	A	A	97	7.1	A	A	95	6.3	A	A	A	A	10	1 x 10 ⁵
Comp. 7	Comp. 1	A	C	92	5.6	B	D	80	4.0	B	C	D	C	25	1 x 10 ⁵
Comp. 8	Comp. 2	B	C	89	5.0	-	-	-	-	C	C	D	D	None	None

[0063]

[Effect of the Invention]

As described so far, the magnetic toner of the present invention is excellent in transferability at
5 high density, provides high-definition images accurately even in a region of low potential on the image-bearing member, and has less soil on the sleeve, image-bearing member and the like. The toner can also be applied fully to image forming methods and apparatus
10 in which the developing step also functions as the cleaning step to recover a portion of the toner remained on the image-bearing member.

[0644]

According to the present invention, images with
15 high quality and resolution as well as demonstrating excellent performance for fog and transferability can be obtained by using a special developer having inorganic fine powder and electroconductive fine powder on its surface with less isolated magnetic powders and
20 average circularity of 0.920 or more, preferably average circularity of 0.950 or more, and more preferably 0.970 or more in combination with the amorphous silicon-based image-bearing member.

[0645]

25 Using the developers of the present invention, the image-bearing member can be charged satisfactorily overcoming charging blocking caused by adhesion and

mixture of the transfer residual toner onto the contact charging member in the image forming method comprising the contact charging method and the magnetic mono-component development method, as well as in the image forming apparatus having the contact charging method, contact transfer method, and toner recycle process, even when the toner is used repeatedly over a long period of time.

[0646]

Using a simple member as the contact charging member, in spite of soil caused by transfer residual toner on the contact charging member, the ozoneless direct injection charging at low application voltage can be maintained in a stable condition for a long period of time, uniform chargeability can be provided, and thereby the image forming apparatus with simple structure with low cost can be realized without any obstacles caused by ozone generation and charging defects.

[0647]

During the long period of repeated use, scars on the image-bearing member caused by the presence of the electroconductive fine powder at the contact position between the charging member and the image-bearing member can be substantially reduced, and thereby being able to prevent image defects.

[Brief Description of the Drawings]

[Fig. 1] A graph showing changes of photosensitive charging potential due to differences of charging methods.

[Fig. 2] An example of a specific apparatus
5 usable for implementing an image forming method according to the present invention.

[Fig. 3] Another example of a specific apparatus usable for implementing the image forming method according to the present invention.

10 [Fig. 4] A schematic view for illustrating an example of a developing device suitable for implementing an image forming method of the present invention.

[Fig. 5] A schematic sectional view for
15 illustrating an example of an image-bearing member usable in the present invention.

[Fig. 6] Another schematic sectional view for illustrating an example of an image-bearing member usable in the present invention.

20 [Fig. 7] A schematic view showing an example of an apparatus for producing an image-bearing member by the RF plasma CVD method using high-frequency power source applicable to the production of the image-bearing member to be used in the present invention.

25 [Fig. 8] A schematic view showing an example of an apparatus for producing an image-bearing member by the VHF plasma CVD method using VHF power source

applicable to the production of the image-bearing member to be used in the present invention.

[Fig. 9] A view for illustrating an example of a contact transfer member suitably used in the present invention.

[Fig. 10] A view for illustrating an example of a photosensitive member comparative to the present invention.

[Description of Reference Numerals or Symbols]

- 10 1 Latent image-bearing member (image-bearing member)
- T Toner (magnetic toner)
- 302 Transfer roller (transfer means)
- 306 Primary charging roller (charging means)
- 15 307 Developing device (developing means)
- 308a, 308b Conveyor roller
- 309a, 309b Transfer entrance guide
- 310 Eliminating needle head
- 311 Conveyor guide
- 20 312 Cleaner
- 312a Cleaning blade
- 312b Screw
- 313 Fixing device
- 313a Fixing roller
- 25 313b Pressure roller
- 313c Heating member of fixing roller
- 313d Fixing roller surface temperature detection

element

- 313e Fixing roller bias voltage application power source
- 313f Fixing separation claw
- 5 L Laser beam
- P Transfer material
- 11a Magnetic blade (layer thickness regulating member)
- 12 Sleeve (toner-carrying member)
- 10 13 Applied magnetic toner
- 14 Fixed magnet roller
- 17 Developing vessel
- 19 Photosensitive drum (image-bearing member)
- 20 Magnetic toner
- 15 21 Alternating voltage power source
- 201 Electroconductive support
- 202 Charge injection barrier layer
- 203 Photoconductor layer
- 204 Surface layer
- 20 205 Charge generation layer
- 206 Charge transport layer
- 2100, 3100 Deposition device
- 2110, 3110 Reaction vessel
- 2111, 3111 Cathode electrode
- 25 2112, 3112 Electroconductive support
- 2113, 3113 Heater
- 2114, 3114 Gas introduction pipe

	2115, 3115	High-frequency matching box
	2116, 3116	Gas pipe
	2117, 3117	Leak valve
	2118, 3118	Main valve
5	2119, 3119	Vacuum gauge
	2120, 3119	High-frequency power source
	2121, 3121	Insulating material
	3122	Insulation shield plate
	2123, 3123	Electroconductive platform
10	2200, 3200	Gas supply unit
	2211 to 2216, 3211 to 3216	Mass-flow controller
	2221 to 2226, 3221 to 3226	Material gas cylinder
	2231 to 2236, 3231 to 3236	Valve
	2241 to 2246, 3241 to 3246	Inflow valve
15	2251 to 2256, 3251 to 3256	Outflow valve
	2260, 3260	Auxiliary valve
	2261 to 2266, 3261 to 3266	Pressure adjuster
	3120	Driving unit
	3130	Discharge space
20	34a	Core metal
	34b	Conductive elastic layer
	35	Transfer bias voltage supply
	100	Photosensitive drum (image-bearing member)

[Name of the Document] Abstract

[Abstract]

[Problem(s)] It is to provide a magnetic toner, image forming method and image forming apparatus, which will
5 not generate discharge product and can reduce waste toner in a substantial amount; enables development and simultaneous cleaning image formation advantageous for compactization at low cost; can obtain good images without causing charging defects during the long period
10 of repeated use; and can be applied to the development and simultaneous cleaning

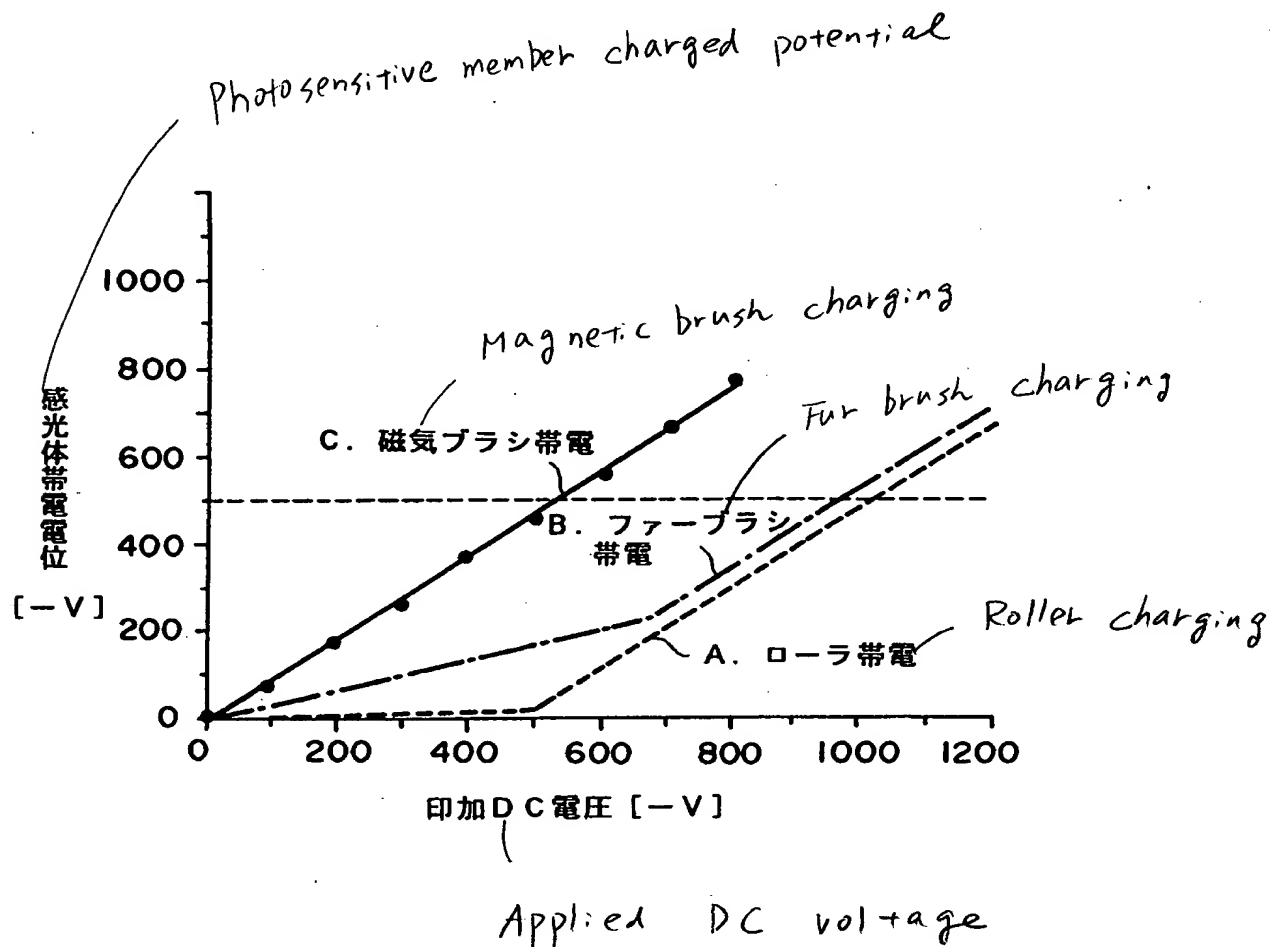
[Means for Solving the Problem(s)] In forming an image where an a-Si-based photosensitive member is charged to 250 to 600 volts in terms of an absolute value by
15 applying voltage to a charging member contacting while forming a contact position with the photosensitive member; an electrostatic latent image is formed; an electrostatic latent image is visualized by transferring a magnetic toner carried on a toner-
20 carrying member to the electrostatic latent member; and a toner image is electrostatically transferred to a transfer material, a magnetic toner comprising at least a binder resin and a magnetic iron oxide, having an average circularity of 0.920 to 0.995, containing 0.05
25 to 3.00 % of isolated iron and iron compounds, and having inorganic fine powder and electroconductive fine powder present at the surface thereof is used.

[Elected Drawing] None

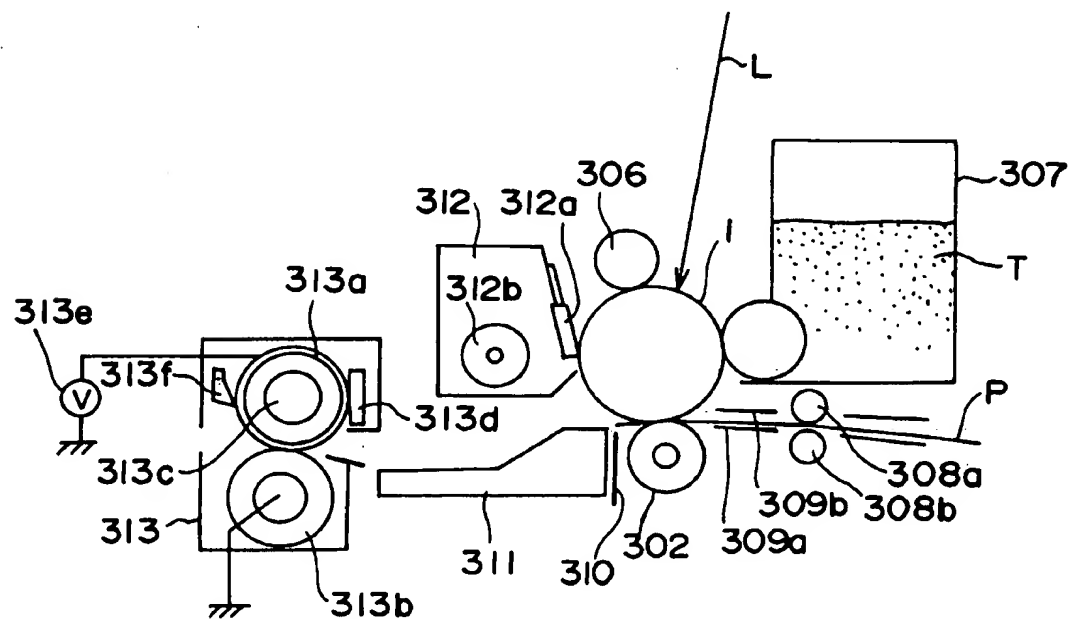
【書類名】 図面 {Name of the Document} Drawings

【図1】

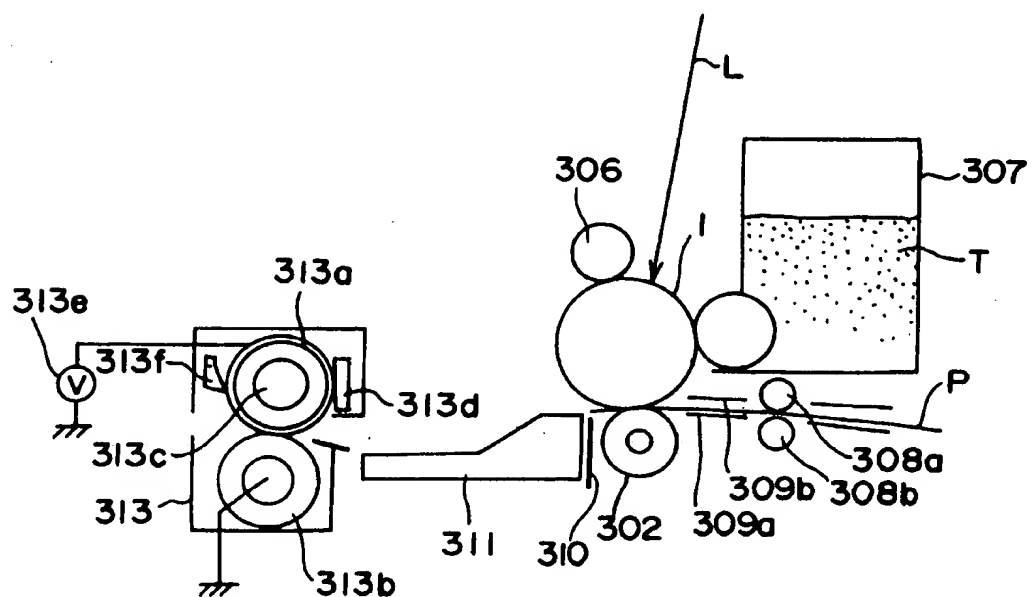
Fig. 1



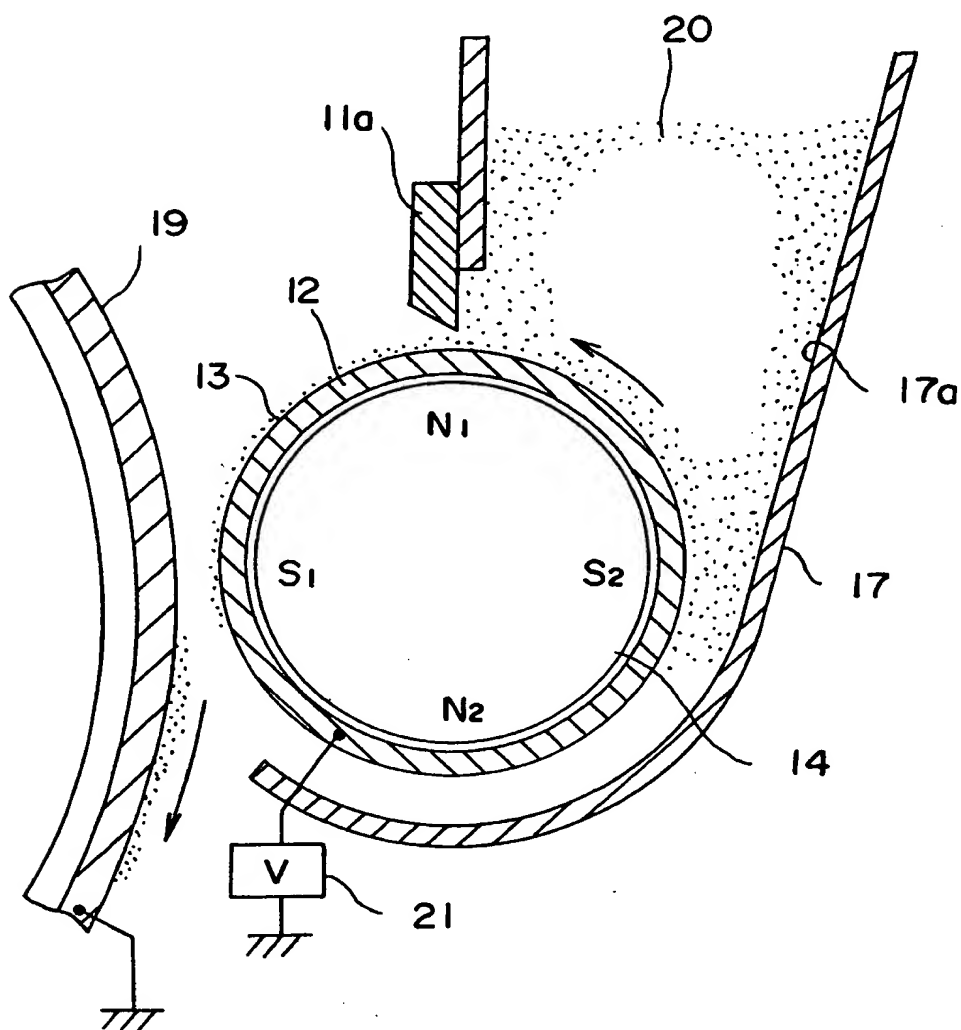
【図2】 Fig. 2



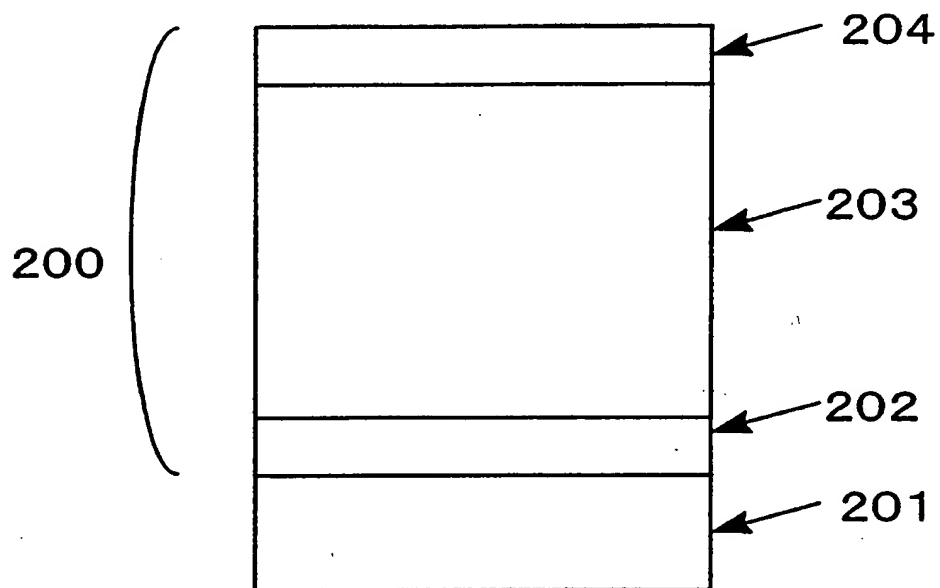
【図3】 Fig. 3



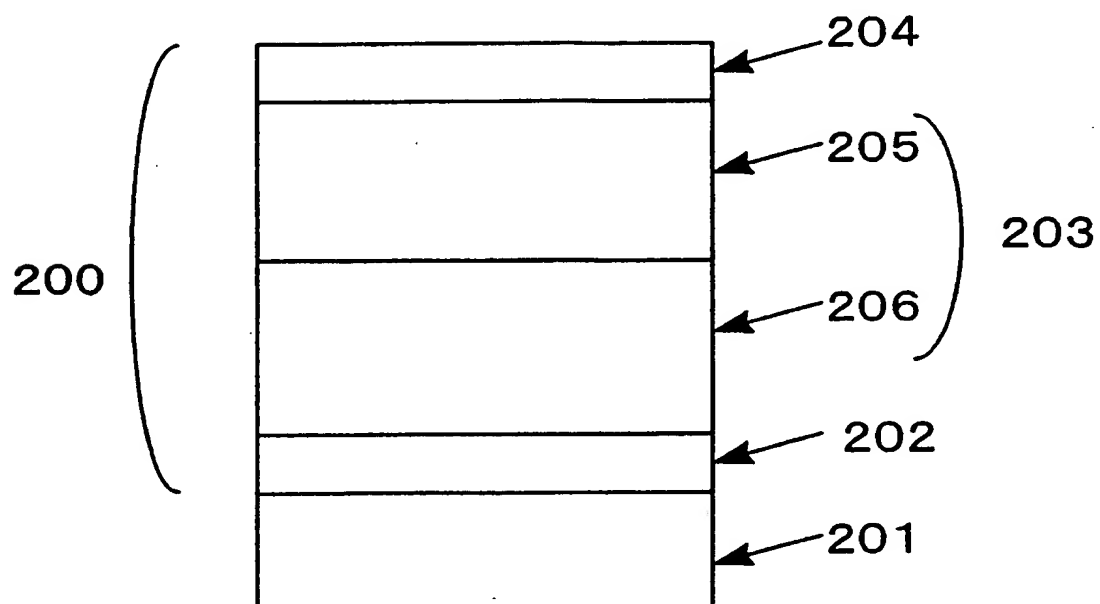
【図4】 Fig. 4



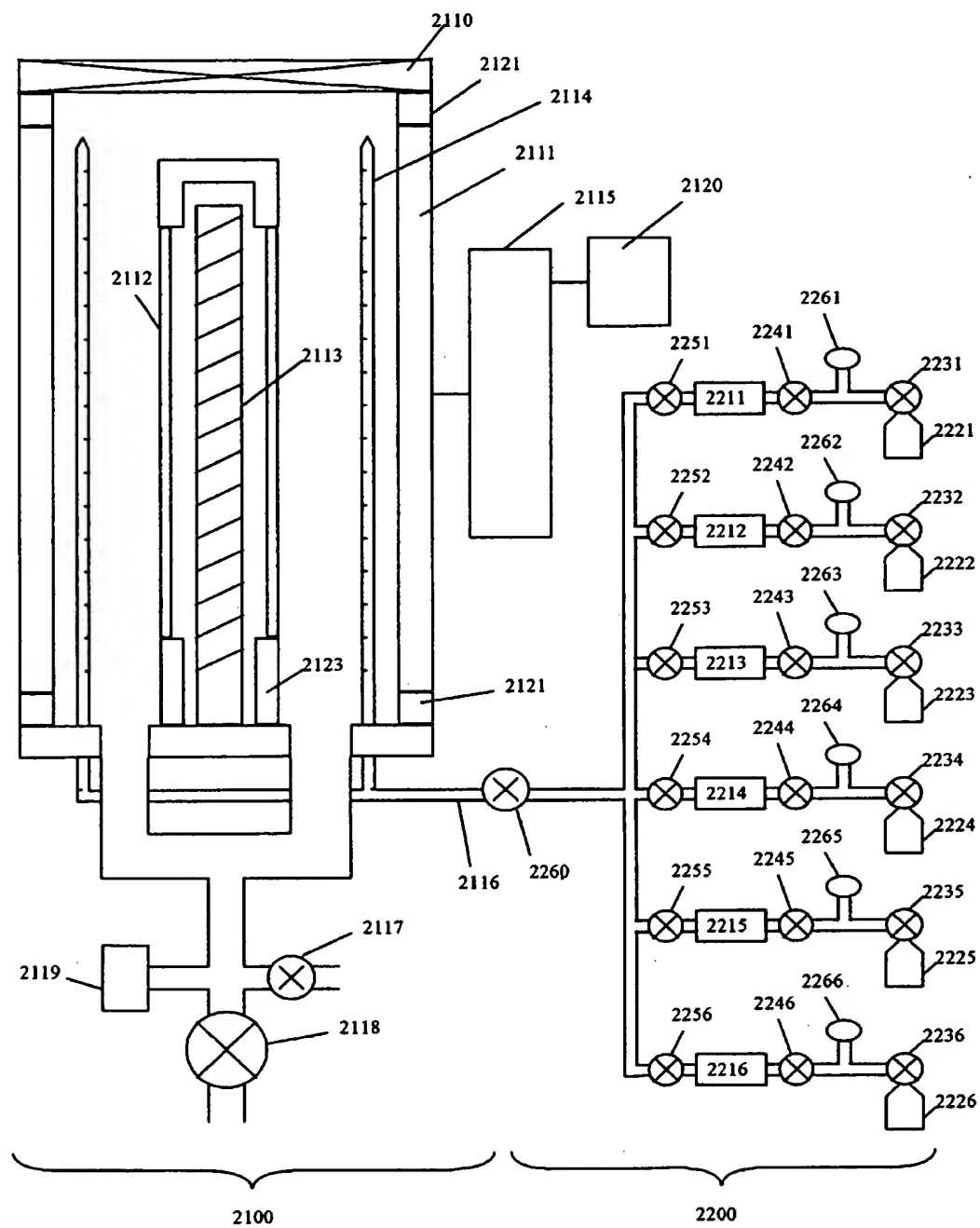
【図5】 Fig. 5



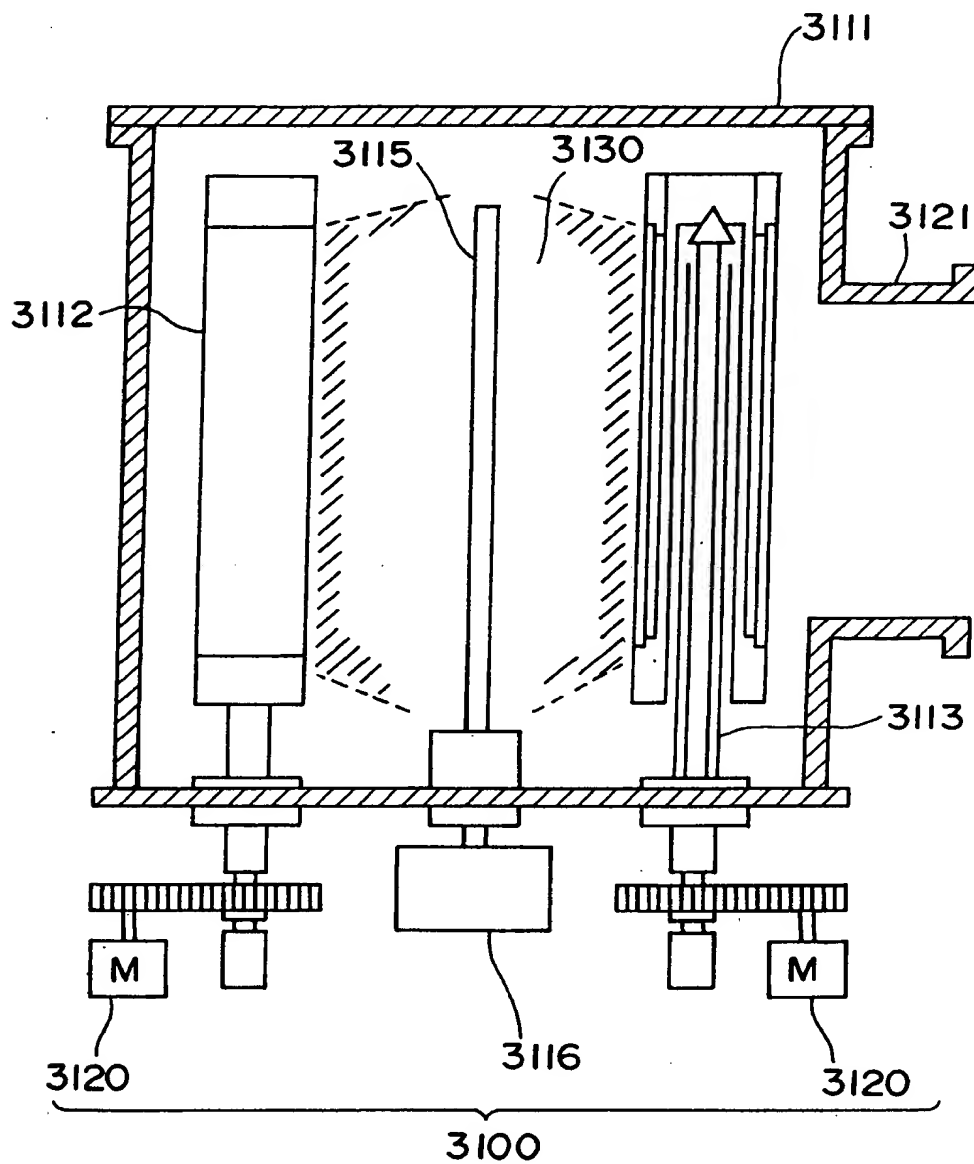
【図6】 Fig. 6



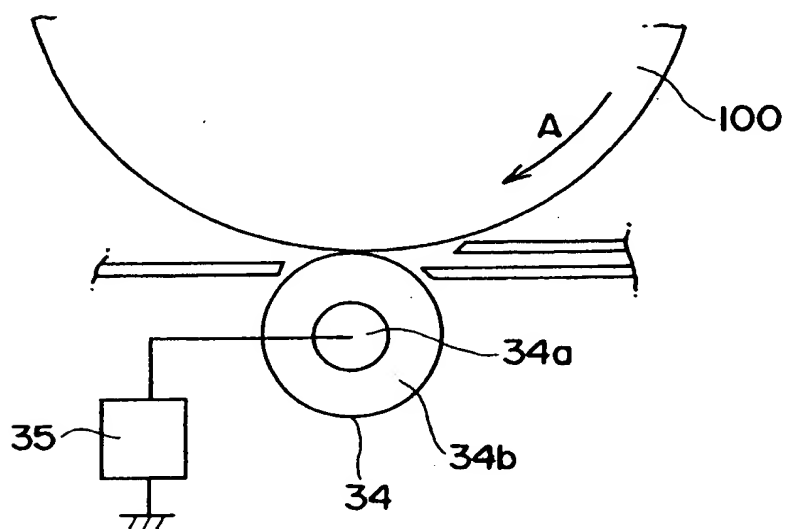
【図7】 Fig. 7



【図8】 Fig. 8



【図9】 Fig. 9



【図10】 Fig. 10

